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EVALUATION OF EPA METHOD 603 (MODIFIED)

by

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16. ABSTRACT

USEPA Method 603 was modified and evaluated with newly established chromatographic conditions for the determination of acrolein, acrylonitrile, and acetonitrile. Method detection limits (MDLs) for the new chromatographic conditions were found to be equivalent to those previously specified in Method 603 for acrolein and acrylonitrile (0.7 and 0.5 µg/L, respectively). The method detection limit found for acetonitrile in this work was 2.7 µg/L.

The method was found to be accurate and precise for the determination of all three method parameters. Recoveries and precisions were determined at two spiking levels in each of three matrices, namely, reagent water, Columbus Publicly Owned Treatment Works (POTW) wastewater, and industrial wastewater. Acrolein was not stable in the industrial wastewater even though the water was buffered at pH 4.5 before spiking. For the other two matrices, the acrolein recovery ranged from 80 to 104% (average, 94%) and the precisions ranged from 1 to 4% relative standard deviation (RSD) (average, 3% RSD). The loss of acrolein due to apparent chemical degradation in the industrial wastewater underscores the current lack of understanding of the chemical factors that control the stability of acrolein in aqueous systems.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, Ohio conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report presents the results of the evaluation of some revisions to Method 603 for the analysis of acrolein, acrylonitrile, and acetonitrile to correct deficiencies in the original methodology. It provides a validated test procedure for the measurement of these substances in wastewater.

Robert L. Booth, Director
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ABSTRACT

EPA Method 603 was modified and evaluated with newly established chromatographic conditions for the determination of acrolein, acrylonitrile, and acetonitrile.

The recommended chromatographic column and conditions specified in the original method were found to be unsuitable when acetonitrile was included as a method parameter. Porapak QS was found to perform well as a gas chromatography (GC) packing for the three method parameters, and method validation using reagent water, Publicly Owned Treatment Works (POTW) outfall, and industrial wastewater was successfully performed.

Method detection limits (MDLs) for the new chromatographic conditions were found to be equivalent to those previously specified in Method 603 for acrolein and acrylonitrile (0.7 and 0.5 µg/L, respectively). The method detection limit found for acetonitrile in this work was 2.7 µg/L.

The method was found to be accurate and precise for the determination of all three method parameters. Recoveries and precisions were determined at two spiking levels in each of three matrices, namely reagent water, Columbus POTW wastewater, and an industrial wastewater. Seven replicates were analyzed for each of the six spike-level matrix sets. For acetonitrile, recoveries for the six sets ranged from 86 to 111 percent (average, 99 percent) with precisions ranging from 3 to 17 percent relative standard deviation (RSD), (average, 11 percent RSD). The corresponding values for acrylonitrile were recoveries ranging from 84 to 104 percent (average, 97 percent) and precisions ranging from 3 to 8 percent RSD (average, 4 percent RSD). Acrolein was not stable in the industrial wastewater even though the water was buffered at pH 4.5 before spiking. For the other two matrices, the acrolein recovery ranged from 80 to 104 percent (average, 94 percent) and the precisions ranged from 1 to 4 percent RSD (average, 3 percent RSD). The loss of acrolein due to apparant chemical degradation in the industrial wastewater

underscores the current lack of understanding of the chemical factors that control the stability of acrolein in aqueous systems. All of the data sets were quantified using both an internal standard method and an external standard method. These two quantification methods provided essentially identical accuracy and precision results.

This report was submitted in partial fulfillment of Contract Number 68-03-1760, Work Assignment Number 5, by Battelle's Columbus Laboratories. The research reported here was conducted under the sponsorship of the U.S. Environmental Protection Agency.

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SECTION 1

INTRODUCTION

The Environmental Protection Agency's Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati, Ohio has primary responsibility for the development and evaluation of monitoring methods for organic pollutants in industrial wastewaters. One of the methods for wastewater monitoring that has been developed by EPA is Method 603. This involves a heated purge-and-trap technique and gas chromatographic analysis for the determination of acrolein and acrylonitrile.

This method validation study was undertaken in response to prior experience of various laboratories which suggested that Method 603 was not a reliable analysis method. For example, a previous single laboratory method validation study performed for EPA by another contracting laboratory produced no useful data. In addition, several investigators have querried EPA regarding difficulties with the reproducibility of the gas chromatography and problems encountered from acetone interference. Thus, development and use of improved chromatographic conditions was a critical first step in this work.

In an effort to increase the usefulness of Method 603, EPA has contracted Battelle Columbus Laboratories, under Contract Number 68-03-1760, to conduct a research program to: 1) recommend modifications to Method 603 for improving the GC of analysis; 2) evaluate the feasibility of including acetonitrile as a method parameter; and 3) validate the method as modified using three matrices (reagent water, POTW wastewater and a relevant industrial wastewater) and two spiking levels (a "low" level near the MDL and a "high" level at least 10-fold higher than the "low" level.)

SECTION 2

CONCLUSIONS

The validation data contained in this report support the following conclusions regarding the performance of Method 603 for the determination of acetonitrile, acrolein, and acrylonitrile:

- No apparent advantage is gained by the use of an internal standard calibration procedure. However, the quality assurance feature of an internal standard may have merit in some cases.
- Both of the previously recommended GC columns are unsuitable for the separations needed if acetonitrile is to be included as a method parameter. A Porapak QS column provides the required separation of all three analytes.
- The method appears to be precise and accurate for acetonitrile determination even though the purging efficiency of acetonitrile is only about 50 percent.
- Factors that affect acrolein stability in aqueous samples are still not well understood.

SECTION 3

RECOMMENDATIONS

Based upon the results of the evaluations conducted under this research program, the following recommendations are made:

- The method should be revised to include Porapak QS as the primary GC packing. Chromosorb 101 should remain a recommended alternate packing only for samples for which it is known that either acrolein or acetonitrile is absent.
- Acetonitrile should be included in the parameter list of the method since the data collected indicate that this compound can be determined with good precision and accuracy.
- Further evaluation of the conditions which affect the stability of acrolein in aqueous samples should be conducted.

SECTION 4

EXPERIMENTAL

APPARATUS

The following equipment was employed in this research program.

GC:	Varian 1400; FID detector
Purge-and-Trap Apparatus:	Tekmar Model LSC-2
Purge Vessel:	Standard 5-mL vessel with glass frit bottom as provided by Tekmar (No. 14-0042-024) or Supelco (No. 2-2424)
Heater Purge Bath:	1-liter beaker containing 0.9 liter water and a 2-inch magnetic Teflon-coated stirbar. A stirring hot plate, controlled by a Variac was used to maintain 85 $\pm$ 2°C. The temperature was monitored by a calibrated digital thermometer.
GC-Tekmar Interface:	The Tekmar heated transfer line was connected to the packed column injector inlet so that the usual syringe/septum injections could be performed without disturbing the Tekmar connections. There were no unheated transfer line sections.
Chromatography Data System:	All validation data were processed using a Computer Inquiry Systems, Inc. (CIS) Computer Automated Laboratory System (CALS). All signal

intensity/time data were archived on 9-track tape.

REAGENTS

The following are the reagents and chemical supplies used to this work.

Reagent Water:	Reagent water was prepared by passing boiled water from a Milli-RO/Milli-Q system through a column (40 cm x 2.8 cm ID) containing granular activated carbon with integral 300-mL reservoir. The column reservoir was protected from laboratory air with a drying tube filled with the same activated carbon.
Granular Activated Carbon:	Barneby and Cheney Type PC, Lot 2547
Acetonitrile:	Burdick and Jackson, No. 15 (UV grade), Lot AJ543
Acrolein:	Aldrich No. 23,954-2, 99+%, Lots 2511JK and 1311TE
Acrylonitrile:	Aldrich No. 11,021-3, 99+%, Lot 2020HK
1-Chloropropane:	Aldrich No. C6,855-5, 99% Lot 7718LH
Sodium Citrate:	J. T. Baker, AR Grade, Trisodium Citrate Dihydrate, crystalline
Citrate Buffer Preparation:	A 0.1 M stock solution of pH 4.5 citrate buffer was prepared by adding 5.9 g sodium citrate to 200 mL of reagent water and adjusting to pH 4.5 with 9 M sulfuric acid using a pH meter. The

	buffer was then placed in a clean 500-mL glass bottle and purged overnight with helium at a flow rate of approximately 20 cc/min prior to storage.
Standard pH 4.00 Buffer:	Fisher "Certified" No. SO-B-98 Lot 734836-24; Potassium Biphthalate, 0.05 M.

PURGE AND TRAP OPERATING CONDITIONS

The following purge and trap operating conditions were employed:

Purge Vessel Temperature:	85 ± 2°C; water bath
Purge Conditions:	20 mL/min helium; 15 min; trap temperature less than 30°C
Trap Desorption Conditions:	Flow controlled helium GC carrier (30 mL/min); 180°C for 1.5 min
Trap Bake Conditions:	20 mL/min helium; 210°C for 10 min
Six-Port Valve and Transfer Lines:	130°C

During the 1.5 min trap desorption, the spent sample was used to rinse the condensate from the upper section of the purge vessel and was then removed by suction using a separate 5-mL gas tight syringe reserved for that purpose. The purge vessel received no other rinse between samples. The 5-mL sample transfer syringe (Glenco, No. K260-250-2200) was rinsed after each use with reagent water. When not in use for transferring a sample, the all-glass syringe barrel was kept in an oven at 110°C and the syringe plunger and valve and Luer assembly was kept under running reagent water. At the end of each day, the purge vessel was replaced with a clean one from the 110°C oven, and the Tekmar purge-and-trap apparatus was left in "trap bake" mode overnight with a trap temperature of 150°C.

METHOD 603 MODIFICATIONS

Four modifications to Method 603 (1) were made prior to the initiation of the method validation studies. These modifications are those which were evaluated in Task 3 of this contract entitled, "Evaluation of Office of Solid Waste Methods 8030 and 8090" (2), and include:

- Addition of acetonitrile as a third parameter of the method
- Use of a different GC column and GC conditions
- Use of different trap desorption and bake-out conditions
- Improvement of the method for making stock solutions from neat reagents

All other procedures specified in Method 603 were observed for the method validation work. The 1982 revision of Method 603 appears in the appendix. The modified procedures and analysis conditions are described below.

GC Analysis Conditions

Column:	10 ft x 2 mm ID, glass; packed with Porapak QS, 80/100 mesh
Carrier:	Helium at 30 $\pm$ 3 mL/min, flow controlled
Temperature Program:	110°C, 1.5 min (during trap desorption); ballistically to 150°C; isothermal at 150°C for 18 min; ballistically to 190°C for 10 min
Zone Temperatures:	Injector and detector, 200°C

Trap Desorption and Bake-out Conditions

The adsorption trap was desorbed at 180°C for 1.5 minute. The 1.5 minute desorption time began when the trap heater achieved 50°C, and 180°C was achieved on the trap outside surface within 20 sec of that time. The trap bake conditions were 210°C for 10 min at the same flow rate (20 mL/min) as that used for sample purging.

Preparation of Standards

Acetonitrile, Acrolein and Acrylonitrile--

All standards were prepared from 2.00 mg/mL aqueous stock solutions. Each day that analyses were performed, the acrolein stock solution was prepared from neat reagent immediately prior to use. The neat reagents (20.0 mg) were measured volumetrically using 25- or 50-µL syringes (Hamilton Company, Reno, Nevada) into reagent water in a 10-mL volumetric flask which had been underfilled by the amount of neat reagent to be added (25.5 µL, 23.7 µL, and 24.8 µL for acetonitrile, acrolein, and acrylonitrile, respectively). The syringes used were gravimetrically calibrated (± 0.2 mg) to the volume required to deliver 20.0 mg, and they were used only for the preparation of standards throughout the entire study. The neat reagent was added to the water with the flask in a horizontal position so added reagent could not rise to the water/air interface. The flask was then stoppered and shaken thoroughly before returning to an upright position to prevent loss of volatile reagent to the air. Immediately after preparation, the stock solutions were bottled headspace-free in 1.8-mL screw-cap vials with Teflon-faced septa seals and stored on ice or at 4°C until use. Standards were always prepared from previously unused 1.8-mL vials of 2.0 mg/mL aqueous stock. Calibration standards containing all three analytes were prepared on the day of use from the 2.0 mg/mL aqueous stock solutions using microliter syringes and 10-mL volumetric flasks. The water used for preparing standards was boiled Milli-RO/Milli-Q reagent water. Immediately after preparation, such calibration standards were bottled headspace-free, as above, and kept on ice until use. Purged calibration standards spanning the 100-fold calibration range (see chart, following page) were prepared by adding the appropriate amounts of spiking concentrate to 5.0 mL of reagent water in the 5-mL sample transfer syringe (Glenco No. K260-250-2200 with valve and Luer fitting and adjustable plunger seal). Vials of calibration spiking stock were discarded when their use had resulted in 100 µL or more of head space in the vial.

1-Chloropropane Internal Standard--

Stock solutions of 1-chloropropane internal standard (IS) were prepared in methanol by adding 337 µL (via a 500 µL syringe) of 1-chloropropane to 8 mL of methanol in a 10-mL volumetric flask followed by dilution to 10.0 mL and mixing. The methanol stock (30 mg/mL) was immediately bottled headspace-free as described above for later use. Aqueous spiking solution of the internal standard was prepared each day just prior to use. Initially, aqueous IS spiking solutions were prepared from the methanol stock using a 10-mL volumetric flask using the procedure described above for calibration standards. However, poor reproducibility was obtained on the first data set

Preparation of Calibration Standards from Spiking Stock Solutions

Calibration Standard Level, µg/L*	Concentration of Spiking Stock, mg/L*	Volume of Spiking Stock Used for 5.0 mL Water
2/1/1	1/0.5/0.5	10 µL
6/3/3	1/0.5/0.5	30 µL
20/10/10	10/5/5	10 µL
60/30/30	10/5/5	30 µL
200/100/100	10/5/5	100 µL

* Analytes are listed in the following order: acetonitrile/acrolein/acrylonitrile.

(see Section 5, Reagent Water Validation) and all other data sets employed the following IS spiking stock sample preparation procedure. To 5.0 mL of boiled, headspace-free reagent water in a 5-mL gas tight syringe fitted with a valve (Glenco, described above) was added 5.0 µL of the 30 mg/mL IS methanol stock. The syringe contained a Teflon O-ring for mixing the headspace-free standard. The internal standard spiking solution (30 µg/mL) was kept on ice through the day. Each 5-mL sample or calibration standard was fortified with 5.0 µL of this aqueous internal standard by addition from a 5-µL syringe directly into the 5-mL syringe containing the sample or

standard. Samples and calibration standards were mixed before injection into the purge vessel using a 0.2 to 0.3 mL air bubble which was also injected into the purge vessel. Prior to each use of the internal standard spiking solution, about 100 µL was expelled from the 5-mL syringe containing it to assure that the spiking solution remained headspace-free.

LINEAR DYNAMIC RANGE OF THE DETECTOR

In a prior related program (2) for EMSL the linear dynamic range (LDR) of the gas chromatographic system was determined for acetonitrile, acrolein and acrylonitrile using the same GC conditions as those for the work reported here. The experimental details of that work are briefly summarized here since those LDR results are discussed in Section 5.

Aqueous standards for direct injection were prepared the day of use from individual 2 mg/mL aqueous stock solutions (described above) using syringes and 10-mL volumetric flasks. Reagent water (Milli-RO/Milli-Q) was used without buffering or pH modification. The standards were bottled headspace-free in 1.8 mL vials with Teflon-lined septa seals and stored on ice during use. Each vial was sampled through the septum only once or twice to avoid headspace accumulation. Due to the number of analyses required to span the range of interest, the low end and high end of the tested dynamic range were generated on separate days. The first day concentrations were 0.0, 0.5, 1.0, 2.0, 4.0, 15.0, and 50 µg/mL. On the second day, the levels were 0.0, 4.0, 15.0, 50, 100, 250, and 500 µg/mL. The 4.0, 15.0 and 50 µg/mL samples were analyzed in quadruplicate each day while all others were analyzed in triplicate. Each standard contained 1-chloropropane internal standard at the 15 µg/mL level. All injections were 2.0 µL, and the analysis order was randomized.

METHOD VALIDATION

Method validation for Method 603 consisted of the analysis of seven replicates each of reagent water, Columbus POTW outfall, and an industrial wastewater, all of which were spiked at two levels with acetonitrile, acrolein, and acrylonitrile. The low level reagent water determinations were used for calculating the MDL (3).

Sample Acquisition

Columbus POTW Sample--

Aqueous secondary outfall from the Columbus Municipal POTW was collected prior to chlorination on an as-needed basis for use in the validation of Method 603. The samples were collected in clean one-gallon glass bottles and stored at 4°C until spiking and analysis.

Industrial Wastewater Sample--

Aqueous treated outfall from a chemical manufacturing plant producing two of the three method parameters was collected outside of the plant at the point where the outfall enters a drainage ditch. The sample was collected and stored as described above.

Reagent Water Validation

The preparation of reagent water samples for Method 603 validation is described below.

Low Spike Level, Reagent Water--

Reagent water was buffered at pH 4.5 with 10.0 mL of 0.1 M sodium citrate buffer in each of two 1-liter volumetric flasks. One flask was mixed and transferred to 40-mL VOA vials (headspace free) for analysis of reagent background levels of the method parameters. The second flask was spiked at the 10.0 µg/L level with acetonitrile and at the 5.0 µg/L level with acrolein and acrylonitrile by the addition of 5.0 µL, 2.5 µL, and 2.5 µL, respectively, of 2 mg/mL aqueous stock solutions (described in Section 4). The spiked sample was mixed and transferred to 40-mL VOA vials (headspace free). All vials were stored inverted in ice in a cooler overnight and analyzed the following day using the GC and purge-and-trap conditions described above.

High Spike Level, Reagent Water--

Reagent water was buffered at pH 4.5 with 10.0 mL of 0.1 M sodium citrate buffer in each of two 1-liter volumetric flasks. One flask was processed as described above for analysis of reagent background levels of the method parameters, while the second was spiked at the 100 µg/L level with acetonitrile and at the 50 µg/L level with acrolein and acrylonitrile by the

addition of 50 µL, 25 µL, and 25 µL, respectively, of individual 2 mg/mL aqueous stock solutions. The spiked sample was bottled, stored overnight and analyzed as described above.

Columbus POTW Wastewater Validation

The preparation of spiked samples for method validation using Columbus POTW outfall is described below.

Low Spike Level, POTW--

The POTW sample was buffered at pH 4.5 by the addition of 500 mg of sodium citrate dihydrate to 4 L of the sample and dropwise addition of 9 M sulfuric acid. A pH meter was used to measure the sample pH. Unspiked samples were prepared as described above for sample and reagent background determinations. The low level spiked samples were prepared in a 1-L volumetric flask at the 10 µg/L level of acetonitrile, the 5 µg/L level of acrolein, and the 20 µg/L level of acrylonitrile by the addition of 5.0 µL, 2.5 µL, and 10.0 µL, respectively, of individual 2 mg/mL aqueous stock solutions. The spike sample was bottled, stored overnight and analyzed as described above.

High Spike Level, POTW--

The POTW sample was buffered at pH 4.5 using sodium citrate, and 9 M sulfuric acid and unspiked samples were prepared as described above for sample and reagent background determinations. The high level spiked samples were prepared at the 100 µg/L level of acetonitrile, the 50 µg/L level of acrolein, and the 100 µg/L of acrylonitrile by the addition of 50 µL, 25 µL, and 50 µL, respectively, of individual 2 mg/mL aqueous stock solutions. The spiked sample was bottled, stored overnight and analyzed as described above.

Industrial Wastewater Validation

The preparation of industrial wastewater samples for Method 603 validation is described below.

Low Spike Level, Industrial Wastewater--

Industrial wastewater was buffered at pH 4.5 by the addition of 500 mg of sodium citrate dihydrate to 4 L of the sample and dropwise addition

of 9 M sulfuric acid. A pH meter was used to measure the sample pH. Unspiked samples were prepared and stored for analysis as described above. The low level spiked samples were prepared in a 1-liter volumetric flask at the 10 µg/L level with acetonitrile, the 5 µg/L level with acrolein, and the 10 µg/L level with acrylonitrile by the addition of 5.0 µL, 2.5 µL, and 5.0 µL, respectively, of individual 2 mg/mL aqueous stock solutions. The spiked sample was bottled, stored overnight and analyzed as described above.

High Spike Level, Industrial Wastewater--

Industrial wastewater was buffered at pH 4.5 with sodium citrate and 9 M sulfuric acid, and unspiked samples for background determinations were prepared as described above. High level spiked samples were prepared in a 2-liter volumetric flask at the 100 µg/L level of acetonitrile, the 50 µg/L level of acrolein, and the 100 µg/L level of acrylonitrile by the addition of 100 µL, 50 µL, and 100 µL, respectively, of individual 2 mg/mL aqueous solutions. The spiked sample was bottled, stored overnight, and analyzed as described above.

SECTION 5

RESULTS AND DISCUSSION

GC CONDITIONS

In prior work (1) investigations were conducted to identify a GC column which would effectively provide analysis capability for the three method parameters. Since the specific results of those investigations are provided elsewhere (1), only a summary is presented here. Both of the columns specified in the 1982 revision of Method 603 were unacceptable: (1) Chromosorb 101 resulted in exact coelution of acrolein and acetonitrile and partial resolution of acetone from acrylonitrile but, otherwise, it performs adequately for acrolein and acrylonitrile in the absence of acetonitrile; (2) Durapack CW400/Porasil C resulted in coelution of acetone and acrolein and such severe peak tailing that low level injections (~100 ng) did not provide usable data. Other column packings were tried and the following results obtained were: 1 percent SP-1000/Carbopack B (moderate tailing and acrolein-acetone coelution); 0.1 percent CW 400/Carbopack C (inadequate retention and severe peak tailing); and Chromosorb 104 (high temperature of elution, unacceptable isothermal elution time for acetonitrile and moderate tailing). The column packing used in this work (Porapak QS) was the only one tested which provided baseline separation between the method analytes as well as two potential interferences of interest to EPA (acetone and methylene chloride) and also provided good GC peak shape at low levels. Example chromatograms illustrating the performance of Porapak QS in this study are included in the discussion of the method validation results which follow.

PURGE AND TRAP CONDITIONS

In the previous work cited above, some experiments were performed to compare method performance using the trap desorption conditions

recommended by the 1982 version of Method 603 and those used for this work which were recommended by EMSL. In summary, the conditions used gave improved peak heights for acetonitrile and acrolein and better reproducibility due, apparently, to the more rapid delivery of trapped analytes to the GC column thereby producing narrower and taller GC peaks. Actual recoveries, however, were about the same for the two conditions. The trap bake temperature of 210°C was employed since it is generally desirable that the trap bake temperature be higher than the desorption temperature. The low (100°C) desorption temperature specified in the 1982 version of Method 603 was required by the initial GC column temperature of 45°C and the sensitivity of Durapak CW 400/Porasil C to the presence of liquid water on the column which would be caused by rapid trap heating to 180°C. The Porapak QS column packing is not susceptible to problems caused by liquid water since the initial column temperature is 110°C and macroreticular phases are generally not susceptible to damage caused by water.

LINEAR DYNAMIC RANGE OF THE DETECTOR

Experiments to define the linear dynamic range of the GC system were performed in the related work cited earlier (1). Experimental details of that study are provided in Section 4, and the present section summarizes the results of that work. The statistical results for the external standard approach (raw peak areas) are presented in Table 1 for the range tested (0.5 to 500 µg/mL). The linear regression results for each of the three method parameters over the full range and the lower range are presented in Table 2. Plots of the regression lines are also shown for all three parameters for the full concentration range in Figures 1 through 3. The data set of Table 1 represents 42 injections of standards and 6 injections of blanks which were performed on two different days. Thus, the precision values shown in Table 1 for the 4.0, 15.0, and 50 µg/mL standards (which were repeated on each day and provided overlap for the two ranges) combined data obtained from different calibration standards on separate days and the higher relative standard deviations (RSDs) for those mixed data sets is, therefore, not surprising. When the data are processed by the internal standard method, the

percent RSD values of these combined data sets were reduced by about a factor of 2.0. For example, for acrylonitrile, the internal standard method percent RSDs were 8.1, 8.0, and 9.4 percent for the 4.0, 15.0, and 50 µg/mL levels, respectively, compared to the corresponding values of 22, 22, and 20 percent in Table 1. In general, the regression line analysis results shown in Table 2 and Figures 1 through 3 show excellent linearity of the GC system and FID detector over three orders of magnitude.

METHOD VALIDATION

Reagent Water Validation

The results of replicate analysis of the low level spiked reagent water samples are presented in Table 3 with external standard quantification and in Table 4 with internal standard quantification. The RSDs for the external standard method data (Table 3) were 8.9, 4.3, and 2.8 percent, respectively, for acetonitrile, acrolein, and acrylonitrile, and 9.1, 4.5, and 2.8 percent, respectively, for the internal standard calibration method (Table 4).

The calculated MDL values for acetonitrile, acrolein, and acrylonitrile were 2.7, 0.7, and 0.5 µg/L, respectively, using the external standard method, and comparable values were obtained with internal standardization. These MDL values for acrolein and acrylonitrile are in good agreement with those presented in the 1982 edition of Method 603 which is reproduced in the Appendix.

The results of replicate analyses of the high level spiked reagent water samples are presented in Table 5 with external standard quantification and in Table 6 with internal standard quantification. The average recoveries ranged from 103 to 111 percent for the external standard method, and the precision (RSD) was less than 11 percent in all cases.

For the internal standard calibration method (Table 6), the results are less accurate and precise. The average recoveries range from 111 to 118 percent and RSDs range from 14 to 22 percent. The higher level of inaccuracy and imprecision results from the manner in which the internal standard solution used was stored and used. This data set was actually the first one collected after method shakedown was complete, and at that time the internal

standard spiking solution was being stored headspace-free in five 1.8-mL GC vials. Because of the large number of analyses in the data set, each vial was sampled more than once, and it is thought that the imprecision resulted from volatilization during transfer of the stock spiking solution to the individual vials and/or losses due to accumulated headspace in the 1.8-mL vials. For all subsequent data sets, the internal standard was prepared and maintained headspace-free using the improved procedure described in Section 4.

Representative chromatograms for a 10 ug/L calibration standard, an unspiked buffered reagent water sample, a low-level spiked reagent water replicate, and a high level spiked reagent water replicate are presented in Figures 4 through 7, respectively.

POTW Wastewater Validation

The results of replicate analyses of the low level spiked POTW samples are presented in Table 7 with external standard quantification and in Table 8 with internal standard quantification based upon 1-chloropropane. Agreement between the two calibration methods is very good. The RSDs for acrolein and acrylonitrile were less than 5 percent, but acetonitrile had a relatively high value of 14.3 percent. The reason for the lower precision for acetonitrile in all determinations appears to be due to the relatively low purging efficiency of this compound, which is estimated to be 40 to 50 percent.

The results of replicate analyses of the high level spiked POTW samples are presented in Table 9 with external standard quantification and in Table 10 with external standard quantification using calibration standards which were purged from buffered reagent water. No internal standard calibration was performed in this data set due to the inadvertent omission of the internal standard from two of the three calibration standards analyzed. The results from Table 9 showed unusually high recoveries for acrolein, and an evaluation of the response factors indicated the possibility of acrolein decomposition during purging of the calibration standards. Consequently, a new set of calibration standards was analyzed using reagent water buffered (0.1 mM citrate) at pH 4.5. The data from Table 10 indicate that

indeed there was some decomposition of acrolein during purging in the original calibration standards. It is suspected that the pH of the reagent water may have changed due to microbial growth in the activated carbon column, but insufficient data are available to determine this. Upon replacement of the activated carbon, this problem did not recur.

Representative chromatograms of an unspiked buffered POTW sample, a low level spiked POTW replicate, and a high-level spiked POTW replicate are presented in Figures 8 through 10, respectively.

Industrial Wastewater Validation

The results of replicate analyses of the low-level spiked industrial wastewater samples are presented in Table 11 with external standard quantification and in Table 12 with internal standard quantification based upon 1-chloropropane. Although recoveries were good for acetonitrile and acrylonitrile, acrolein was not stable in the sample and was not recovered to any significant extent. The pH of a sample was checked after analyses and found to be 4.5, indicating that there are other factors which affect the stability of acrolein that are not known.

The results of replicate analyses of the high-level spiked industrial wastewater samples are presented in Table 13 with external standard quantification and Table 14 with internal standard quantification based upon 1-chloropropane. Good recoveries were found for acetonitrile and acrylonitrile, but, as for the low spiked samples, acrolein was not recovered to any significant extent.

Representative chromatograms of an unspiked industrial wastewater sample, a low-level spiked industrial wastewater replicate, and a high level spiked industrial wastewater, all buffered at pH 4.5, are presented in Figures 11 through 13, respectively.

The problem of acrolein instability in authentic matrix samples was also observed for the POTW wastewater but not until the sample had aged at 4°C for about five days. The low- and high-level spiked POTW experiments were completed within four days of sampling with apparently good acrolein stability characteristics for both sets of analyses. However, the high-level spiked sample had to be repeated due to a spiking error, and the unused,

buffered aliquots were used to prepare new samples. The pH of the stored sample was found to be 4.2 and was readjusted to pH 4.5 before spiking. Upon analysis the following day, the acrolein (spiked at 50 µg/L) had apparently quantitatively decomposed although the pH remained at 4.5. The experiment was then successfully repeated with a fresh sample of POTW wastewater. Due to the logistical impossibility of resampling the industrial wastewater, it could not be determined whether a fresh sample would have permitted overnight stability for spiked acrolein. The industrial wastewater was iced immediately after sampling and maintained at 0°C or 4°C throughout the time between sampling and analysis. Our speculation at present is that acrolein degradation may be due to microbial activity that occurs after sampling that generates chemical species which degrade acrolein, or that the microbial populations increase upon anaerobic storage to provide an active population of microbes that directly degrade acrolein. Further work is required to fully understand the factors that affect acrolein stability in field samples.

SECTION 6

QUALITY ASSURANCE

Quality assurance measures in effect throughout the program included the following:

- Fresh stock solutions were prepared from neat acrolein on a daily basis due to the instability of this compound.
- Fresh calibration standards for quantification purposes were prepared on a daily basis.
- A system blank consisting of a dry run of the purge-and-trap system and gas chromatograph was the first instrument run of the day. This blank run checked for contamination of the purge-and-trap system and proper operation of the equipment.
- A reagent water blank was run as the second run each day to check on the purity of the water used to prepare the calibration standards.
- The instrument response was calibrated each day prior to the analysis of samples with a minimum of three levels of calibration standards which encompassed the concentration range anticipated for samples to be analyzed.
- Except for one case, at least one calibration standard was analyzed after all sample analyses to verify that the system remained in calibration throughout the analysis period.
- An internal standard was included in each purge-and-trap GC run to monitor the retention times and as a check on the transfer efficiency of sample from purge-and-trap to the GC.

Summaries of the external standard method response factors for acetonitrile, acrolein, and acrylonitrile are presented in Tables 15, 16, and 17, respectively, along with the appropriate statistical information

obtained for any given day's work. The corresponding internal standard method response factors are presented in Tables 18, 19, and 20. Tables 15 through 20 represent all of the response factors used to calculate the recoveries reported. In general, the RSD obtained for response factors on a given day with all calibration levels considered was less than 10 percent for all analytes.

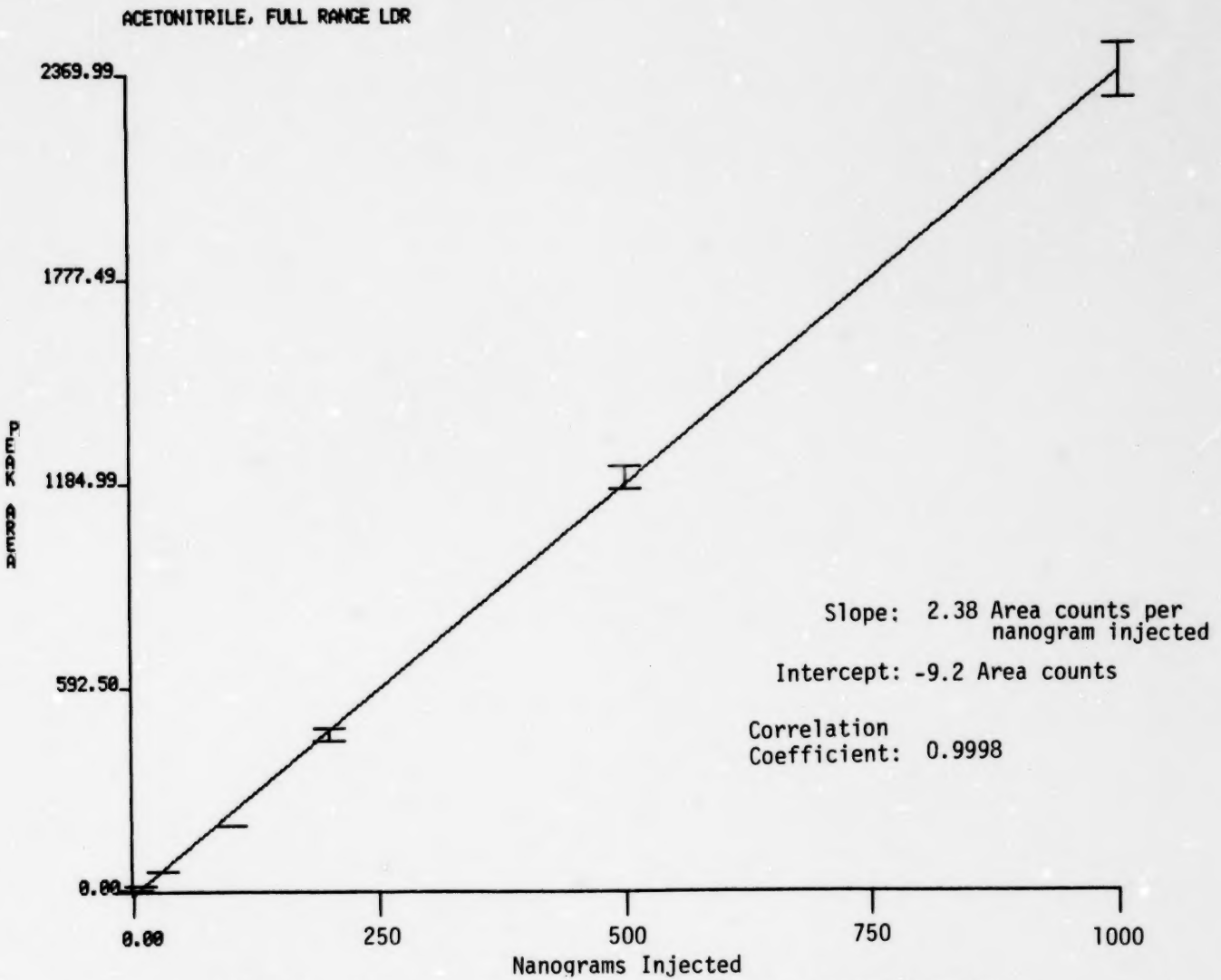

Figure 1. Linear regression analysis plot for linear dynamic range of acetonitrile, 0.5 to 500 mg/L, 2 µL injection.

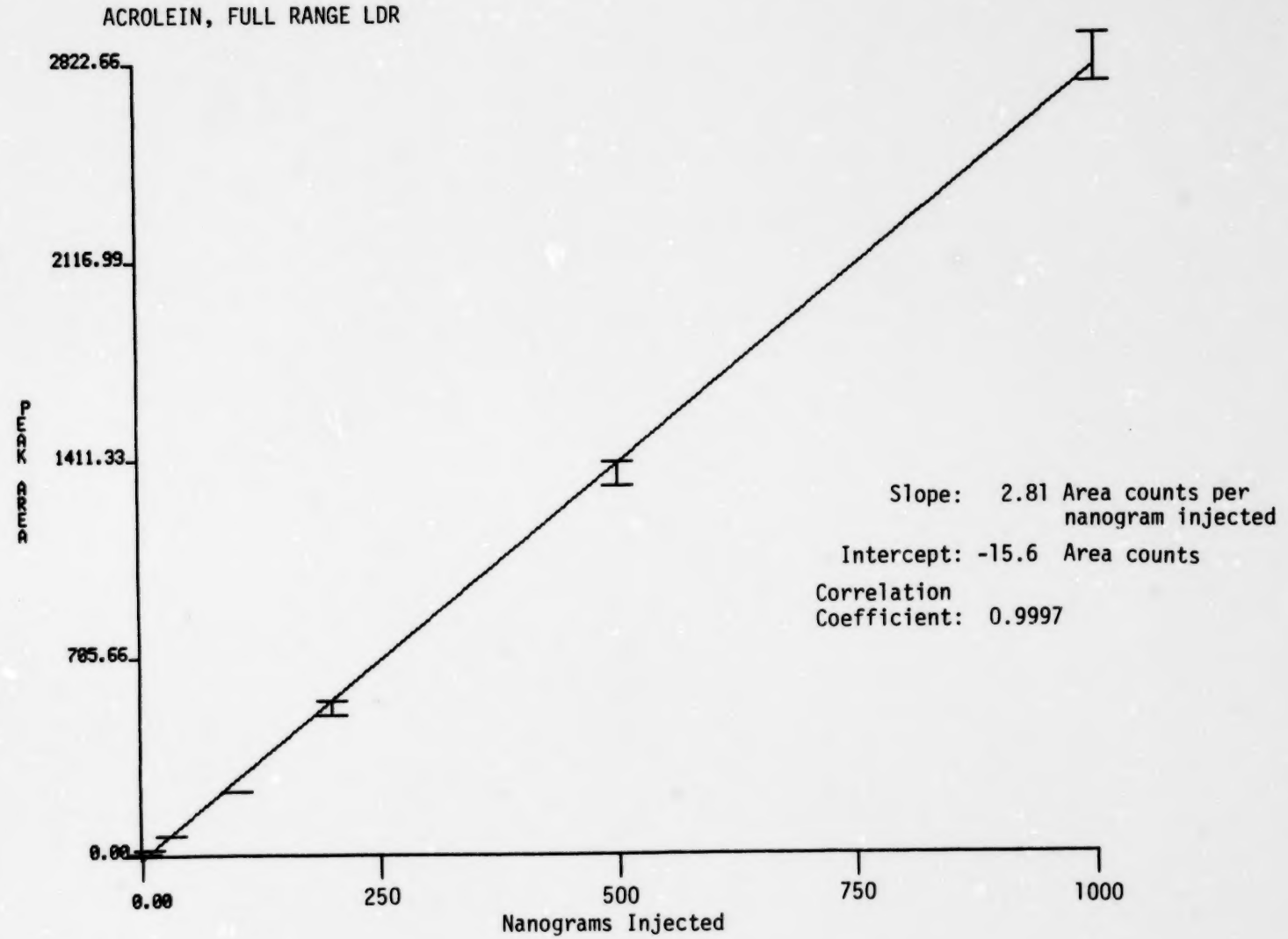

Figure 2. Linear regression analysis plot for linear dynamic range of acrolein, 0.5 to 500 mg/L, 2 µL injection.

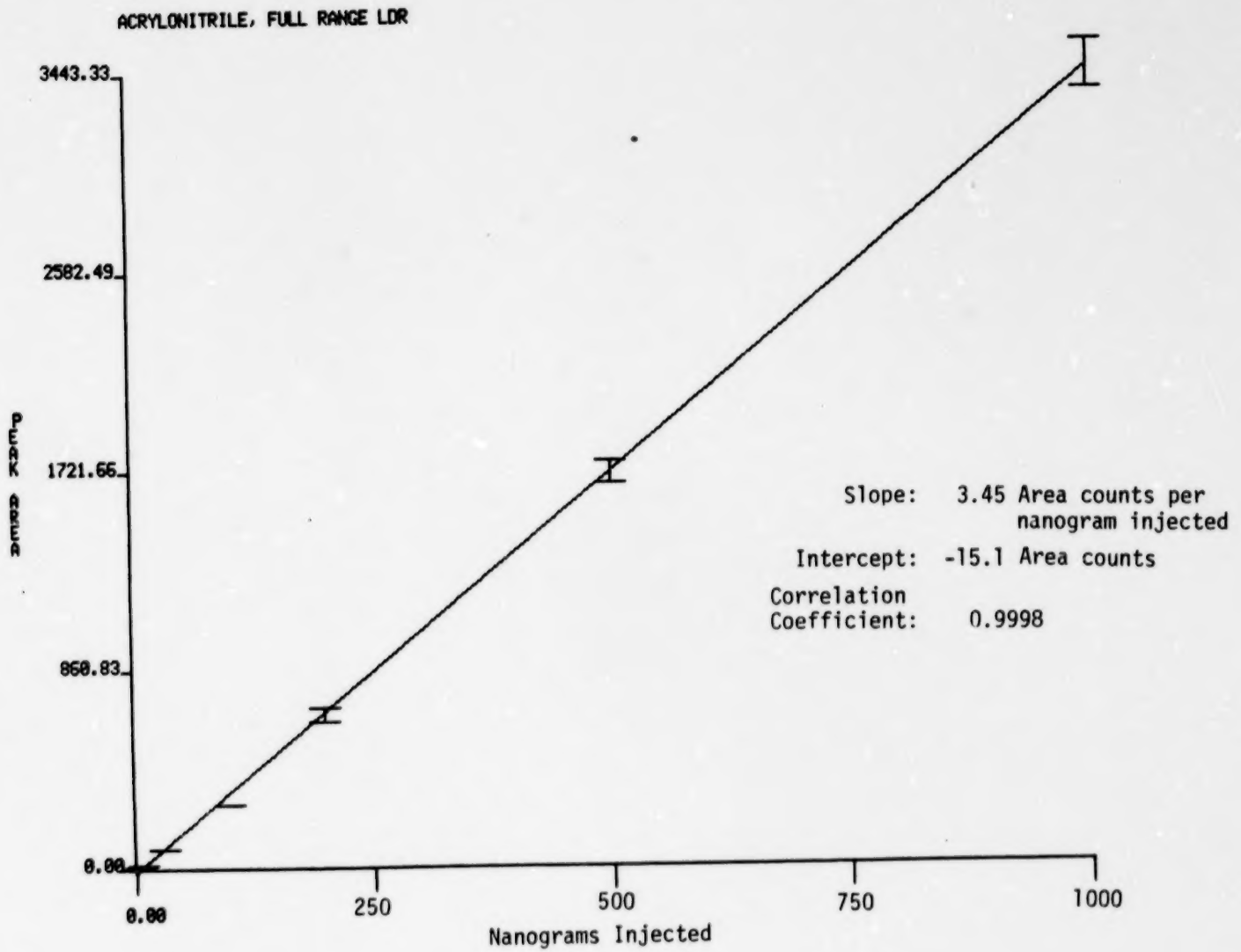

Figure 3. Linear regression analysis plot for linear dynamic range of acrylonitrile, 0.5 to 500 mg/L, 2 µL injection.

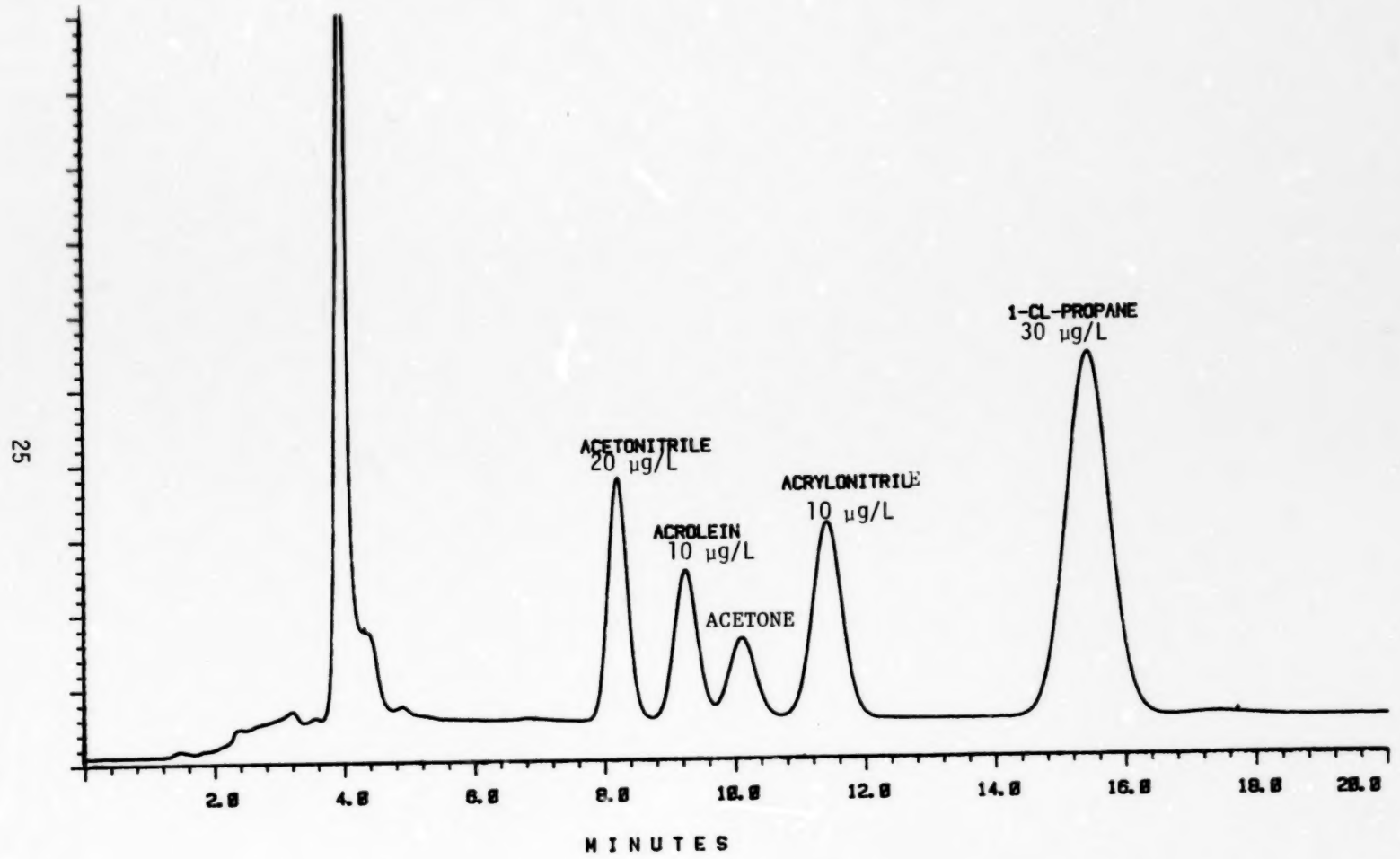

Figure 4. GC-FID chromatogram of a 10 µg/L calibration standard using modified Method 603.

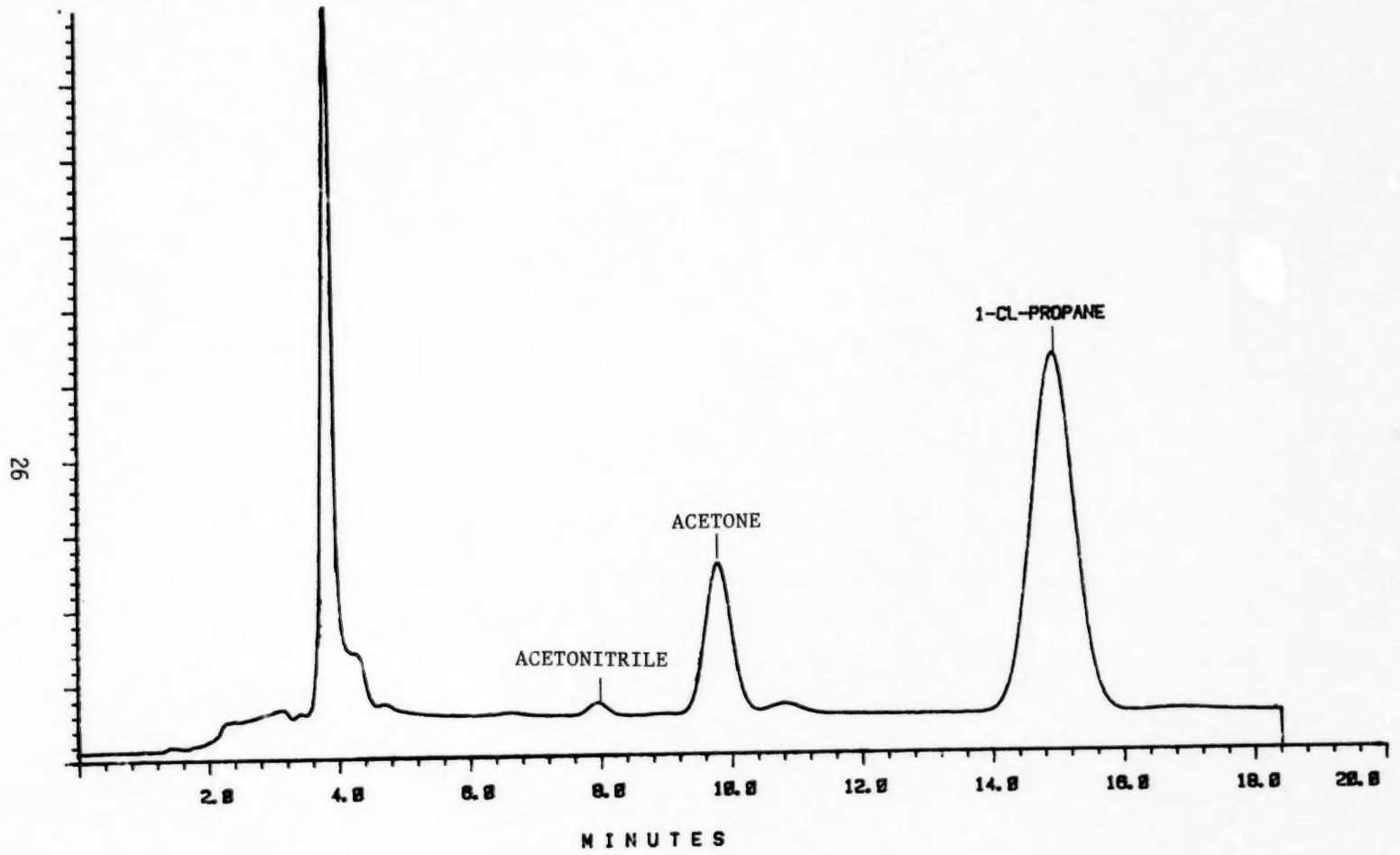

Figure 5. GC-FID chromatogram of unspiked reagent water using modified Method 603.

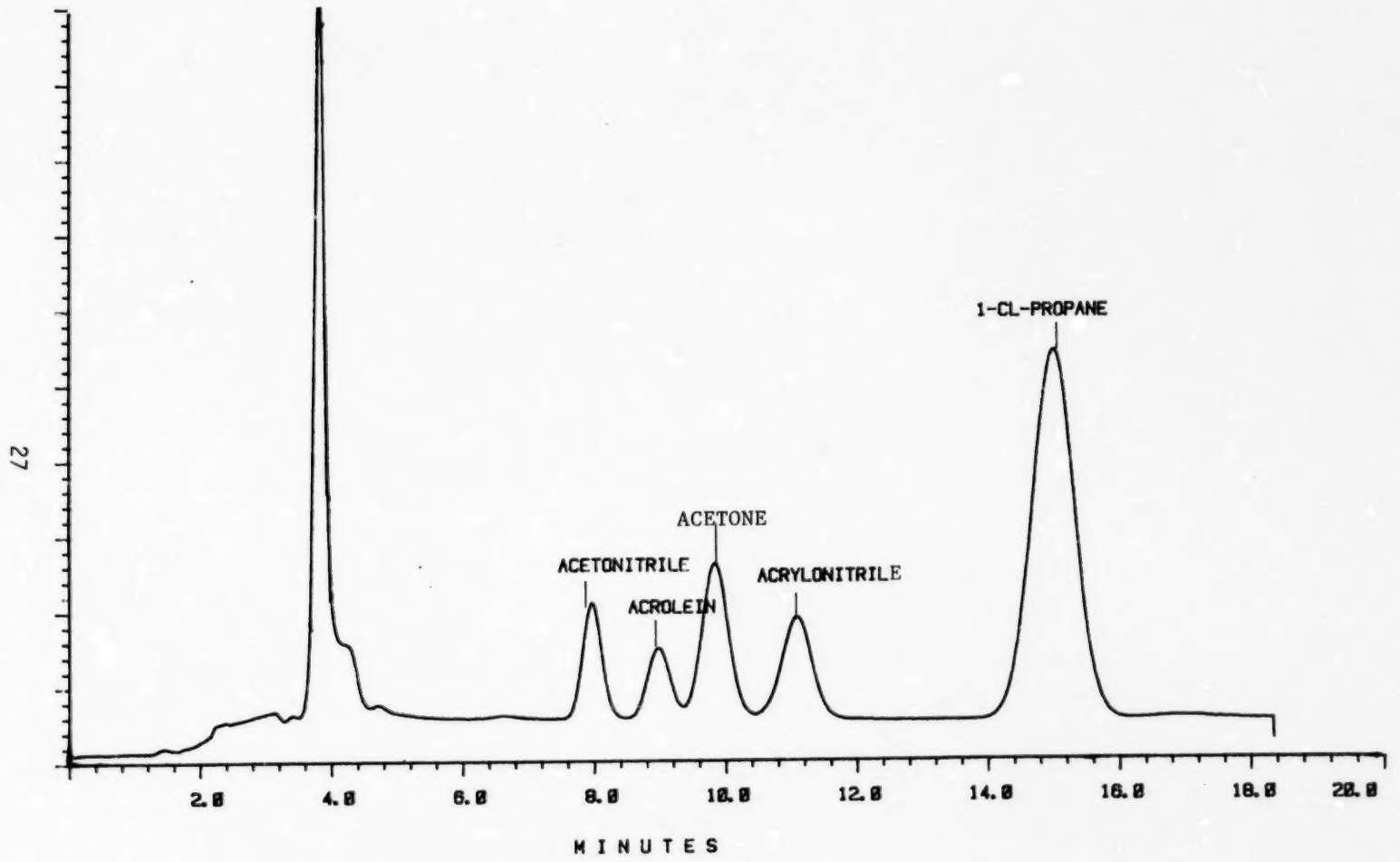

Figure 6. GC-FID chromatogram of low-level spiked reagent water using modified Method 603.

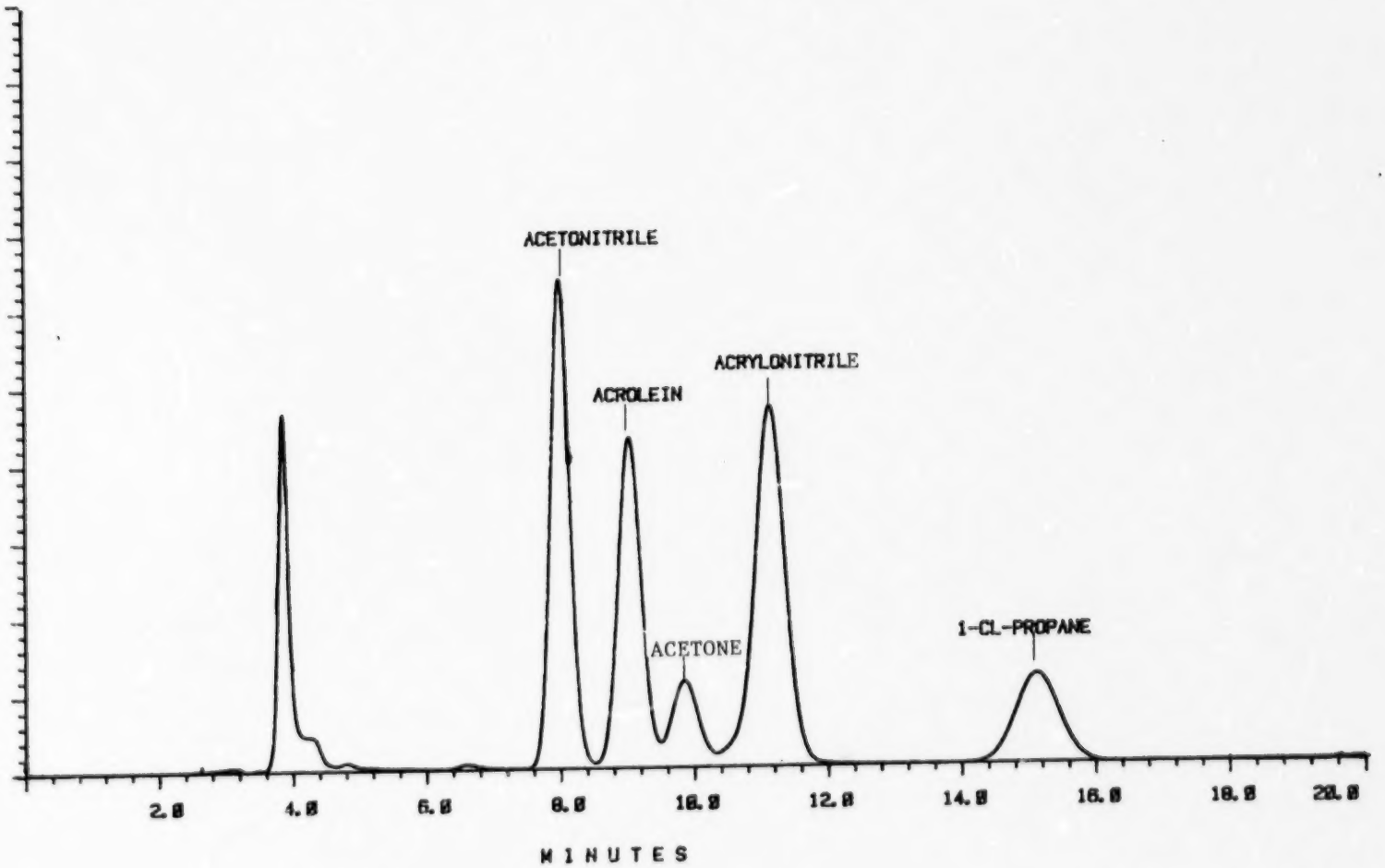

Figure 7. GC-FID chromatogram of high-level spiked reagent water using modified Method 603.

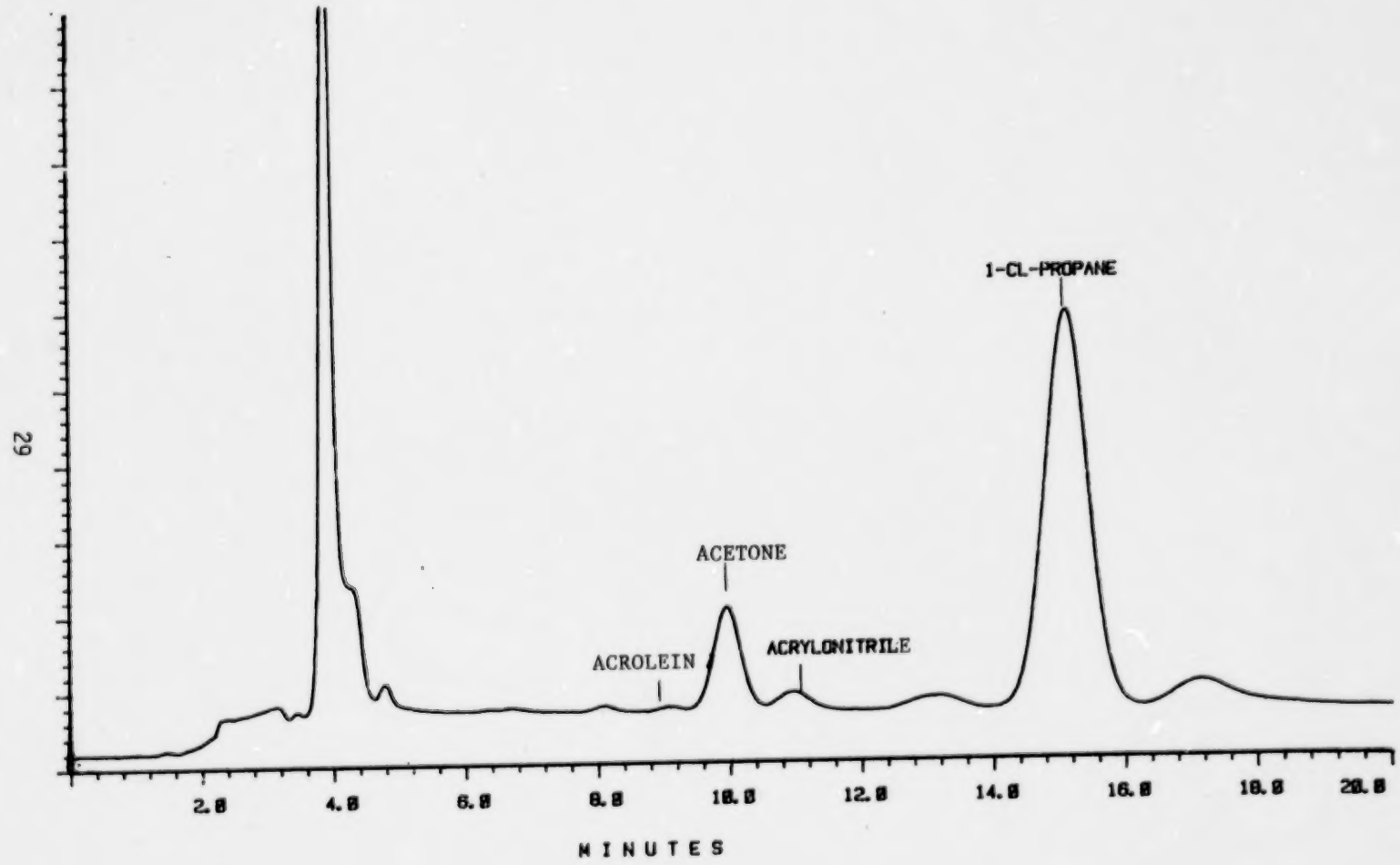

Figure 8. GC-FID chromatogram of unspiked Columbus POTW outfall using modified Method 603.

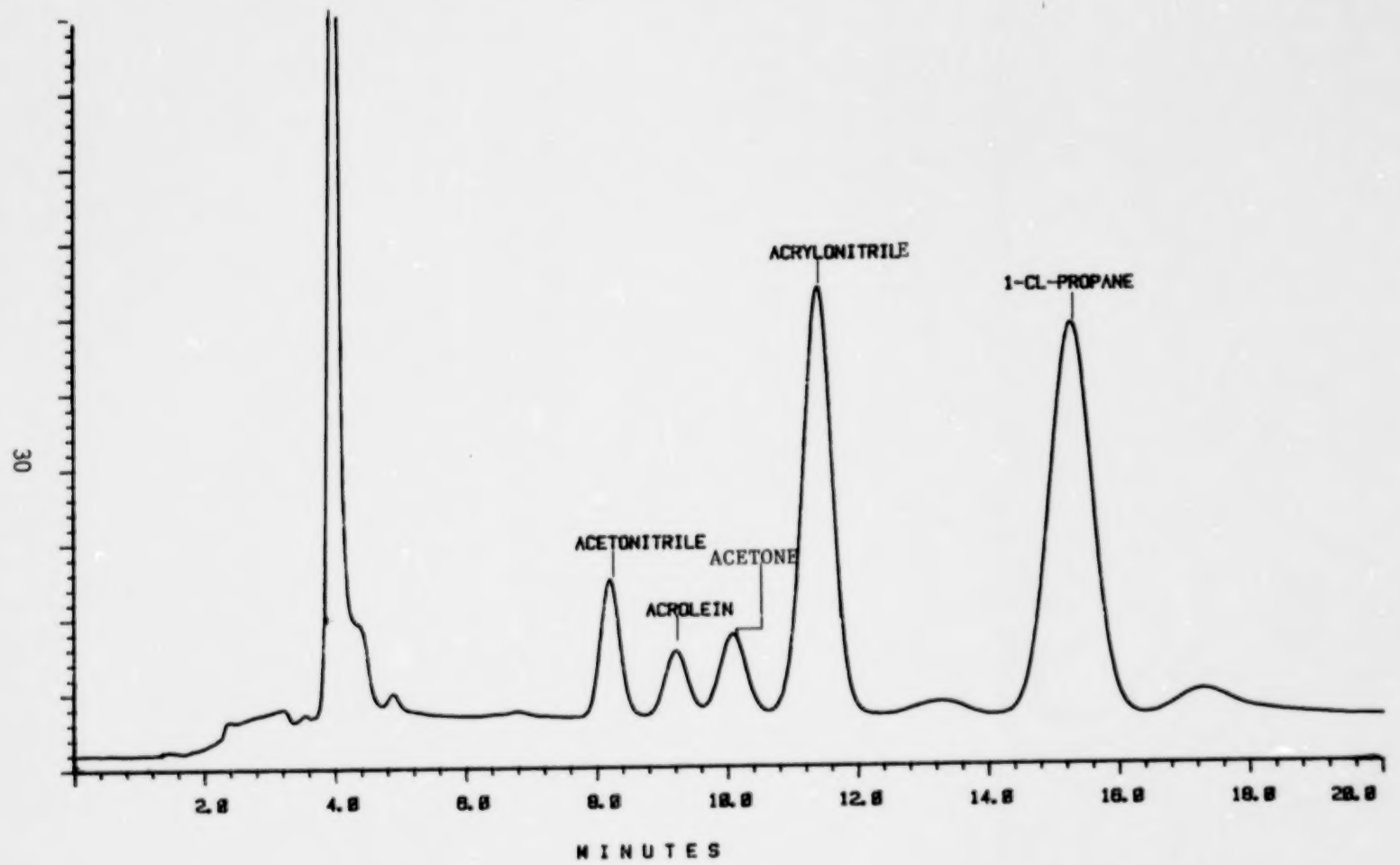

Figure 9. GC-FID chromatogram of low-level spiked POTW outfall using modified Method 603.

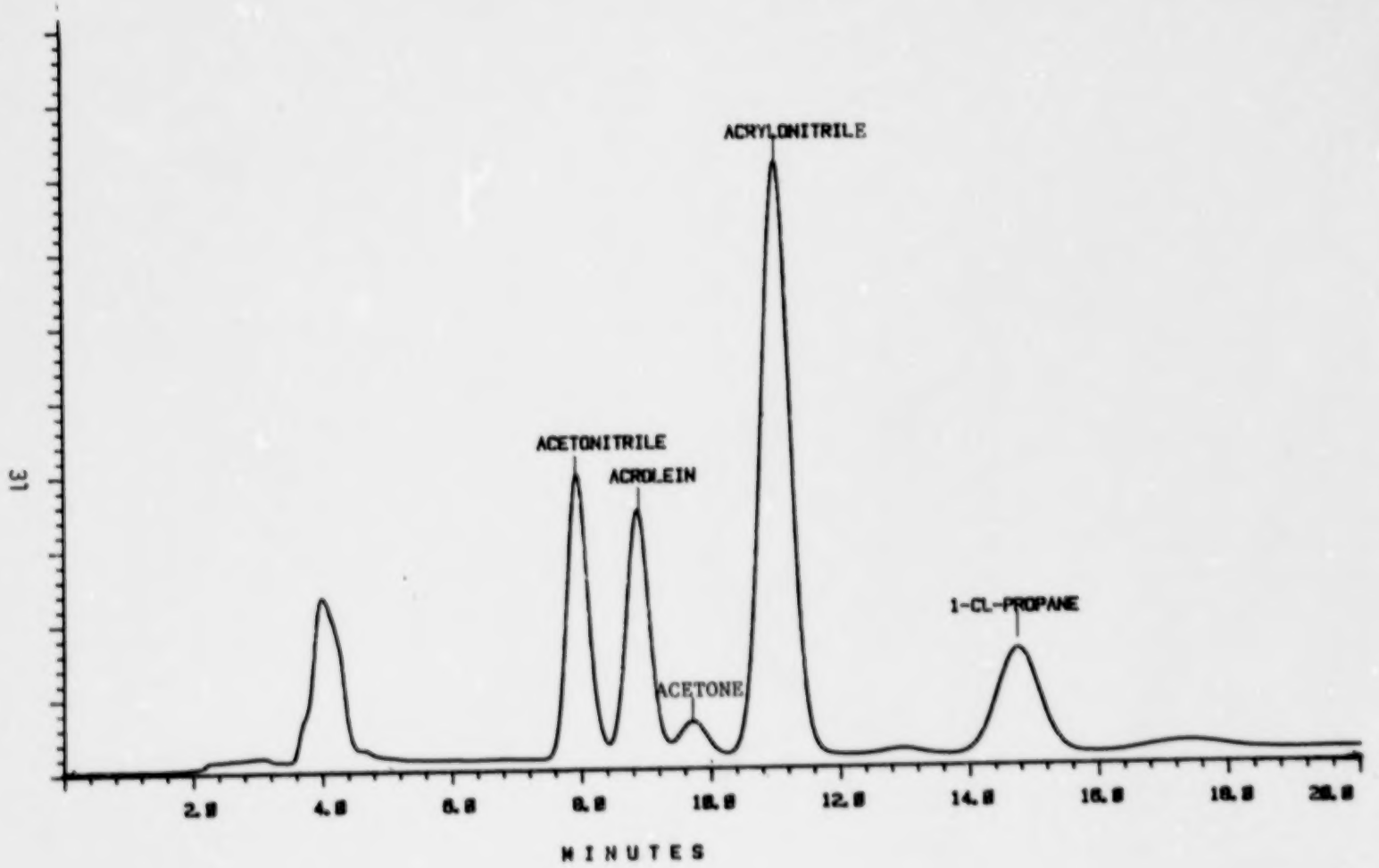

Figure 10. GC-FID chromatogram of high-level spiked POTW outfall using modified Method 603.

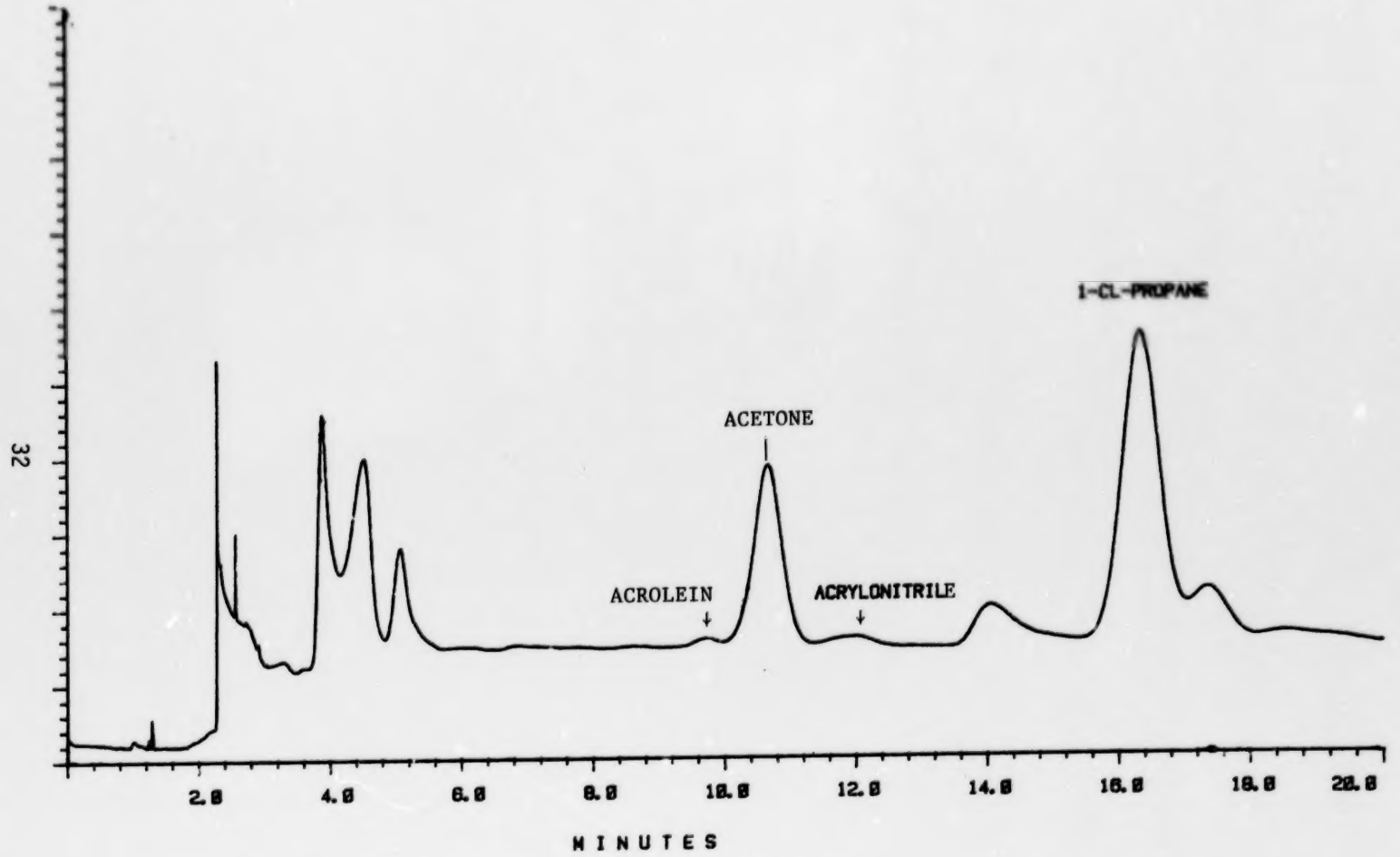

Figure 11. GC-FID chromatogram of unspiked industrial wastewater using modified Method 603.

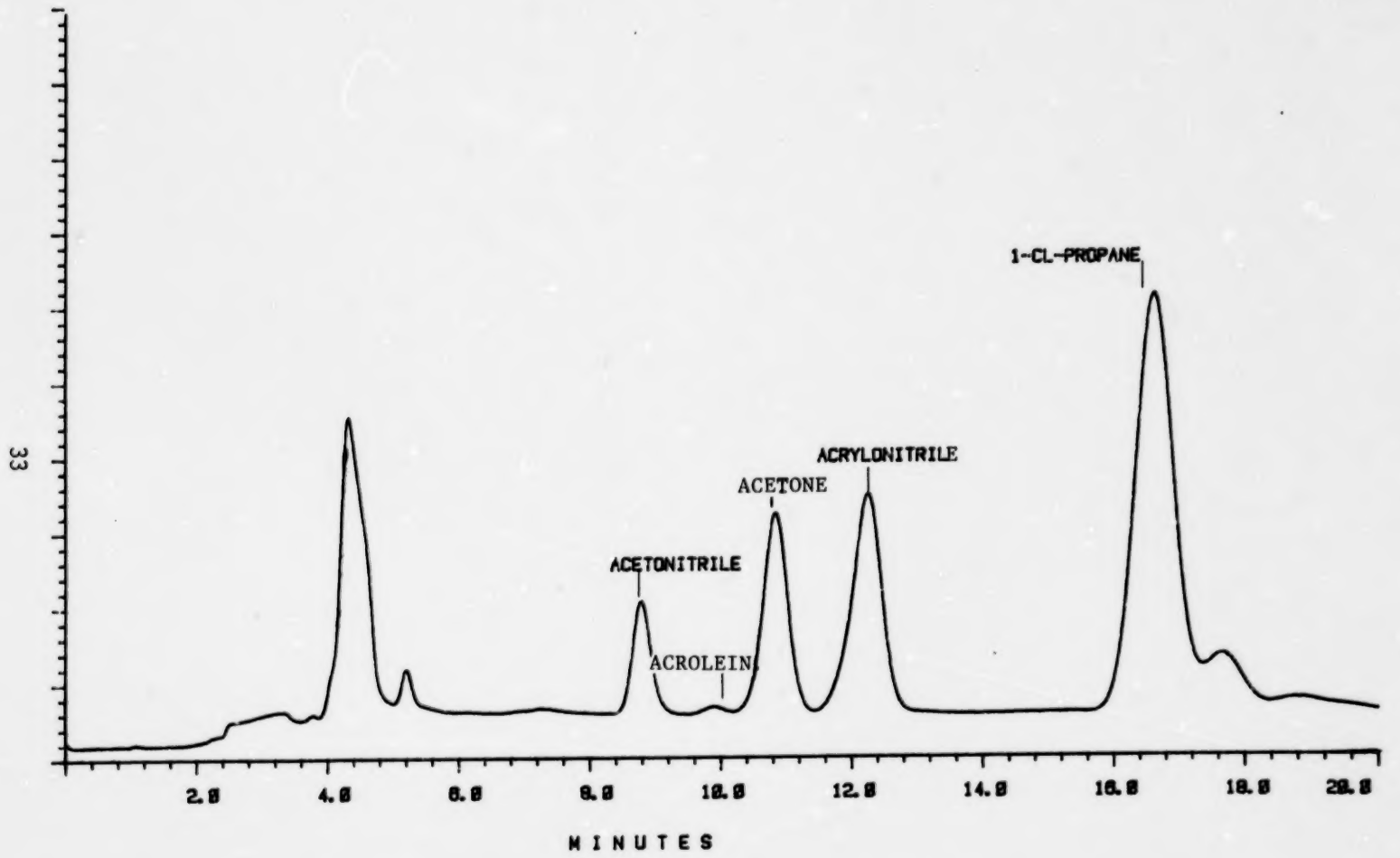

Figure 12. GC-FID chromatogram of low-level spiked industrial wastewater using modified Method 603.

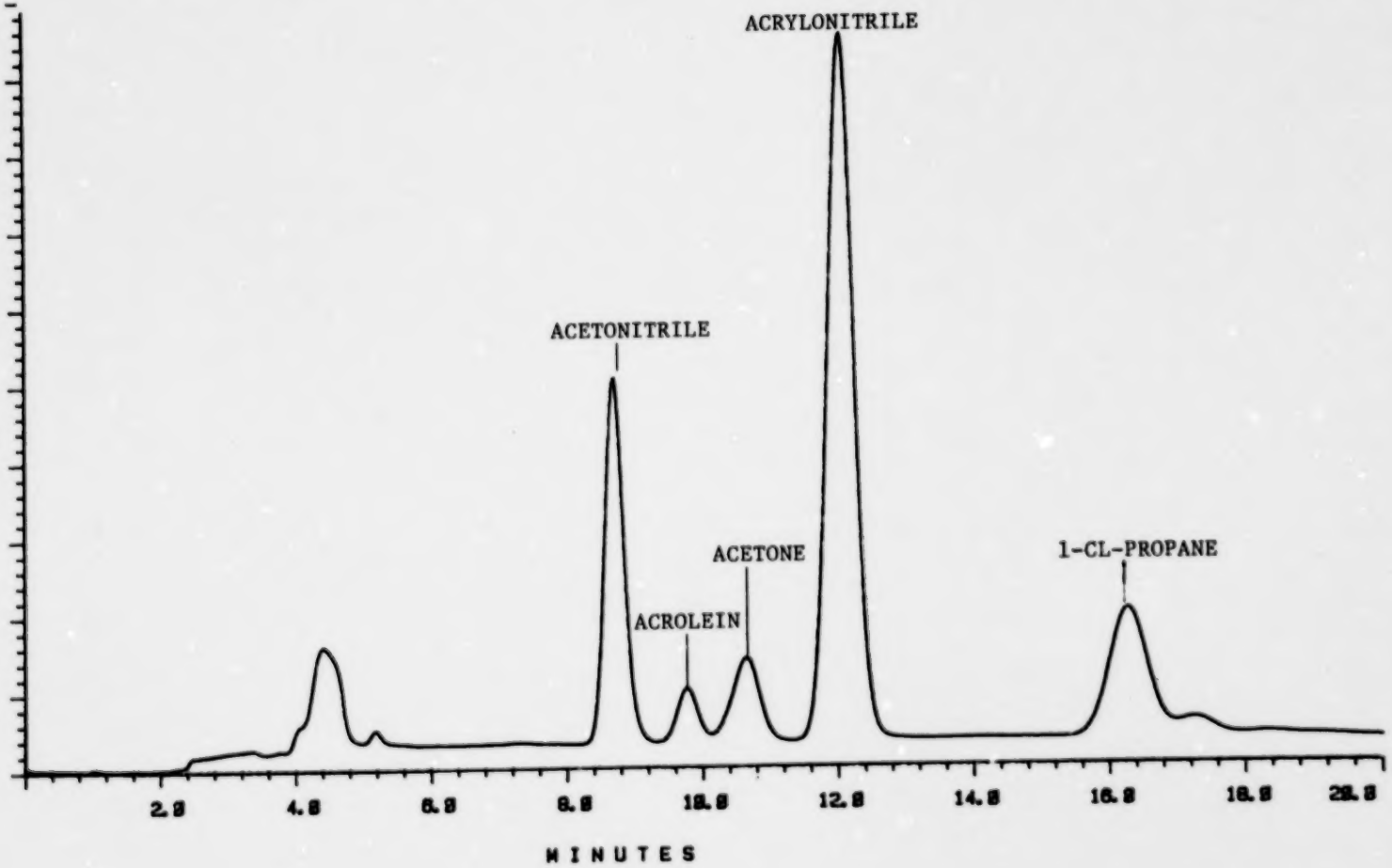

Figure 13. GC-FID chromatogram of high-level spiked industrial wastewater using modified Method 603.

TABLE 1. GC PEAK AREAS FOR THE DETERMINATION OF THE LINEAR DYNAMIC RANGE OF THE DETECTOR--EXTERNAL STANDARD METHOD

Compound	Statistical Parameter	Average GC Peak Area[a] Obtained from 2 µL Injections for the Given Concentration, mg/L								
		0.5[b]	1.0[b]	2.0[b]	4.0[c]	15.0[c]	50[c]	100[b]	250[b]	500[b]
Acetonitrile	Mean	1.39[a]	3.03	6.60	15.7	59	193	456	1200	2370
	Standard Deviation	±0.13	±0.64	±0.09	±2.8	±11	±32	±18	±35	±80
	Relative Standard Deviation, %	9	21	1.3	18	19	16	3.9	2.9	3.4
Acrolein	Mean	2.39	4.17	8.63	19.9	71	225	524	1350	2800
	Standard Deviation	±0.29	±0.58	±0.46	±4.0	±12	±36	±22	±42	±90
	Relative Standard Deviation, %	12	14	5.4	20	18	16	4.2	3.1	3.1
Acrylonitrile	Mean	1.83	3.84	9.03	21.7	84	277	668	1710	3440
	Standard Deviation	±0.32	±0.70	±0.44	±4.7	±18	±55	±31	±50	±110
	Relative Standard Deviation, %	17	18	4.9	22	22	20	4.6	2.9	3.1

(a) Arbitrary units.
(b) Three replicates.
(c) Eight replicates; four on day 1 using calibration standards prepared with the 0.5, 1.0, and 2.0 µg/mL set, and four on day 2 using calibration standards prepared with the 100, 250, and 500 µg/mL set.

TABLE 2. LINEAR REGRESSION ANALYSIS RESULTS OF LINEAR DYNAMIC RANGE ASSESSMENT OF THE GC-FID SYSTEM

	Regression Analysis Parameter[a] for the Given Concentration Range					
	Full Concentration Range[b] (0.0 to 500 mg/L)			Low Concentration Range[b] (0.0 to 50 mg/L)		
Parameter	Slope	Intercept	Correlation Coefficient	Slope	Intercept	Correlation Coefficient
Acetonitrile	4.76	-9.2	0.9998	3.35	-0.37	0.99995
Acrolein	5.62	-15.6	0.9997	3.96	0.43	0.99999
Acrylonitrile	6.90	-15.1	0.9998	4.64	-0.75	0.99995

(a) Slope Units: Arbitrary GC peak area units per mg/L concentration
Intercept Units: Arbitrary GC peak area units
(b) All data from 2.0 μL injection. See Table 1 for the concentrations analyzed.

TABLE 3. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN REAGENT WATER USING EXTERNAL CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L							Average	SD[a]	RSD, %[b]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7				
Acetonitrile	0.9	10.0	11.3	9.1	9.1	8.7	9.7	9.5	9.3	9.5	0.84	8.9	86
Acrolein	0.0	5.0	5.6	5.0	5.1	5.0	5.3	5.3	5.4	5.2	0.22	4.3	104
Acrylonitrile	1.1	5.0	5.6	5.2	5.2	5.2	5.3	5.3	5.2	5.3	0.15	2.8	84

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation

TABLE 4. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN REAGENT WATER USING INTERNAL CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L							Average	SD[a]	RSD, %[b]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7				
Acetonitrile	0.9	10.0	11.7	9.4	9.2	9.2	10.2	9.7	9.5	9.8	0.89	9.1	89
Acrolein	0.0	5.0	5.6	5.0	5.0	5.2	5.4	5.4	5.5	5.3	0.24	4.3	106
Acrylonitrile	1.1	5.0	5.6	5.3	5.1	5.4	5.4	5.3	5.3	5.3	0.15	2.8	84

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation

TABLE 5. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN REAGENT WATER USING EXTERNAL CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L							Average	SD[a]	RSD,[b] %	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7				
Acetonitrile	1.3	100.0	103	117	123	128	113	104	94.7	112	11.9	10.6	111
Acrolein	0.2	50.0	51.2	50.2	51.5	52.2	52.0	52.2	51.7	51.6	0.709	1.37	103
Acrylonitrile	1.0	50.0	51.6	51.4	55.6	53.1	51.8	52.1	51.2	52.4	1.54	2.94	103

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation

TABLE 6. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN REAGENT WATER USING INTERNAL STANDARD CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L							Average	SD[a]	RSD, %[b]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7				
Acetonitrile	1.2	100	92.7	144	127	155	133	96.9	88.3	120	26.8	22.4	118
Acrolein	0.2	50	48.9	65.7	56.7	67.0	65.1	51.6	51.2	58	7.77	13.4	116
Acrylonitrile	1.0	50	47.3	64.5	58.7	65.3	62.2	49.3	48.6	56.6	7.98	14.1	111

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation

TABLE 7. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN POTW[a] WATER USING EXTERNAL CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L								SD[b]	RSD, %[c]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.3	10.0	13.5	10.5	10.7	9.4	10.1	9.4	9.2	10.4	1.5	14.3	101
Acrolein	0.2	5.0	4.5	4.3	4.3	4.2	4.3	4.1	4.0	4.2	0.2	4.0	80
Acrylonitrile	0.9	20.0	22.5	21.2	21.2	20.4	20.8	20.5	20.3	21.0	0.8	3.7	100

(a) POTW = Publicly Owned Treatment Works secondary effluent prior to chlorination.
(b) SD = Standard Deviation
(c) RSD, % = Percent Relative Standard Deviation

TABLE 8. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN POTW[a] WATER USING INTERNAL STANDARD CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L								SD[b]	RSD, %[c]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.3	10.0	13.5	10.4	11.2	9.5	10.1	9.3	9.4	10.5	1.5	14.1	102
Acrolein	0.2	5.0	4.5	4.3	4.4	4.3	4.3	4.1	4.1	4.3	0.2	3.8	82
Acrylonitrile	0.9	20.0	22.6	21.0	22.2	20.8	20.8	20.3	20.9	21.2	0.8	3.9	102

(a) POTW = Publicly Owned Treatment Works secondary effluent prior to chlorination.
(b) SD = Standard Deviation
(c) RSD, % = Percent Relative Standard Deviation

TABLE 9. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN POTW[a] WATER USING EXTERNAL STANDARD CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L									SD[b]	RSD, %[c]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Rep. 8	Average			
Acetonitrile	0.3	100	79.2	98.4	105.1	108.9	97.5	95.4	100.9	97.9	97.9	8.8	9.0	98
Acrolein	0.2	50	58.7	61.2	62.1	60.8	60.7	60.1	61.7	62.0	60.9	1.1	1.9	121
Acrylonitrile	0.9	100	103.9	106.9	108.4	109.1	106.4	106.4	107.9	108.0	107.1	1.6	1.5	106

(a) POTW = Publicly Owned Treatment Works secondary effluent prior to chlorination.
(b) SD= Standard Deviation
(c) RSD, % = Percent Relative Standard

TABLE 10. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN POTW[a] WATER USING EXTERNAL STANDARD CALIBRATION WITH BUFFERED STANDARDS[b]

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L									SD[c]	RSD, %[d]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Rep. 8	Average			
Acetonitrile	0.7	100	79.4	98.6	105.4	109.1	97.7	95.7	101.1	98.2	98.2	8.8	8.9	98
Acrolein	0.1	50	42.8	44.7	45.3	44.4	44.3	43.8	45.0	45.2	44.5	0.8	1.9	89
Acrylonitrile	1.7	100	99.9	102.8	104.2	104.8	102.2	102.3	103.7	103.8	103	1.5	1.5	101

(a) POTW = Publicly Owned Treatment Works secondary effluent prior to chlorination.
(b) Calibration standards prepared in reagent water buffered at pH 4.5 with citrate buffer (see text).
(c) SD = Standard Deviation
(d) RSD, % = Percent Relative Standard Deviation

TABLE 11. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN INDUSTRIAL WASTEWATER USING EXTERNAL CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L							Average	SD[a]	RSD[b] %	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7				
Acetonitrile	1.2	10.0	10.3	11.3	11.3	10.9	11.2	11.0	11.1	11.0	0.35	3.2	98
Acrolein	0.3	5.0	0.6	0.4	0.4	0.5	0.4	0.3	0.3	0.4	0.11	26.7	2
Acrylonitrile	2.1	10.0	11.7	11.8	12.0	12.0	10.3	10.2	10.4	11.2	0.85	7.6	91

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation

TABLE 12. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN INDUSTRIAL WASTEWATER USING INTERNAL STANDARD CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L								SD[a]	RSD, %[b]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	1.1	10.0	10.1	11.0	11.0	9.3	10.9	10.8	10.8	10.6	0.63	6.0	95
Acrolein	0.3	5.0	0.6	0.4	0.4	0.5	0.4	0.3	0.3	0.4	0.11	26.7	2
Acrylonitrile	2.0	10.0	11.5	11.4	11.8	10.3	11.5	11.4	11.5	11.3	0.48	4.2	93

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation

TABLE 13. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN INDUSTRIAL WASTEWATER USING EXTERNAL STANDARD CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L							Average	SD[a]	RSD, %[b]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7				
Acetonitrile	0.3	100.0	78.8	80.8	86.6	105.3	112.9	120.6	107.2	98.9	16.6	16.8	99
Acrolein	0.6	100.0	9.9	11.3	9.3	9.3	11.5	8.4	9.7	9.9	1.1	11.2	9.3
Acrylonitrile	0.8	100.0	100.3	101.8	103.2	106.0	107.9	109.2	104.8	104.8	3.2	3.1	104

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation

TABLE 14. RESULTS OF METHOD 603 VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN INDUSTRIAL WASTEWATER USING INTERNAL STANDARD CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L							Average	SD[a]	RSD,[b] %	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7				
Acetonitrile	0.2	100.0	76.6	78.7	83.6	101.4	104.0	113.8	103.4	94.5	14.6	15.4	94
Acrolein	0.7	100.0	9.6	11.0	9.0	8.9	10.6	8.0	9.4	9.5	1.0	10.9	8.8
Acrylonitrile	0.8	100.0	97.4	99.1	99.5	101.9	99.3	102.9	101.0	100.2	1.9	1.9	99

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation

TABLE 15. EXTERNAL STANDARD CALIBRATION RESPONSE FACTORS FOR ACETONITRILE

Date of Analysis	Calibration Range, µg/L	Response Factor Parameter			
		$\bar{N}$(a)	Average	SD(b)	RSD, %(c)
3/09/84	20-200	5	3.16	0.14	4.3
3/14/84	2-20	5	2.9	0.4	14
3/21/84	2-20	5	2.77	0.14	5.2
3/30/84	20-200	3	3.683	0.3	7.8
4/02/84	20-200	4	4.000	0.4	9.9
4/04/84	2-20	3	3.835	0.16	4.2

(a) Number of calibration standards analyzed on the given day.
(b) SD = Standard Deviation.
(c) RSD, % = Percent Relative Standard Deviation.

TABLE 16. EXTERNAL STANDARD CALIBRATION RESPONSE FACTORS FOR ACROLEIN

Date of Analysis	Calibration Range, µg/L	$\overline{N}$(a)	Response Factor Parameter Average	SD(b)	RSD, %(c)
3/09/84	10-100	5	1.62	0.09	5.2
3/14/84	1-10	5	2.14	0.15	6.9
3/21/84	1-10	5	2.00	0.27	13
3/30/84	10-100	3	2.40	0.09	3.8
4/02/84	10-100	4	2.46	0.11	4.4
4/04/84	1-10	3	2.26	0.15	6.8

(a) Number of calibration standards analyzed on the given day.
(b) SD = Standard Deviation
(c) RSD, % = Percent Relative Standard Deviation.

TABLE 17. EXTERNAL STANDARD CALIBRATION RESPONSE FACTORS FOR ACRYLONITRILE

Date of Analysis	Calibration Range, µg/L	$\overline{N}$(a)	Response Factor Parameter Average	SD(b)	RSD, %(c)
3/09/84	10-100	5	1.21	0.02	1.2
3/14/84	1-10	5	1.16	0.08	7.1
3/21/84	1-10	5	1.1	0.02	1.5
3/30/84	10-100	3	1.40	0.04	3.2
4/02/84	10-100	4	1.44	0.06	4.4
4/04/84	1-10	3	1.26	0.15	12

(a) Number of calibration standards analyzed on the given day.
(b) SD = Standard Deviation.
(c) RSD, % = Percent Relative Standard.

TABLE 18. INTERNAL STANDARD CALIBRATION RESPONSE FACTORS FOR ACETONITRILE

Date of Analysis	Calibration Range, µg/L	$\bar{N}$(a)	Response Factor Parameters		
			Average	SD(b)	RSD, %(c)
3/09/84	20-200	5	1.8	0.3	17(d)
3/14/84	2-20	5	2.2	0.3	13
3/21/84	2-20	5	2.23	0.05	2.4
4/02/84	20-200	4	2.6	0.3	12
4/04/84	2-20	3	2.94	0.11	3.6

(a) Number of calibration standards analyzed on the given day.
(b) SD = Standard Deviation.
(c) RSD, % = Percent Relative Standard Deviation
(d) Internal standard method provided less reliable results for this data set due to a procedural error. See discussion in Section 5, Reagent Water.

TABLE 19. INTERNAL STANDARD CALIBRATION RESPONSE FACTORS FOR ACROLEIN

Date of Analysis	Calibration Range, µg/L	N(a)	Response Factor Parameter		
			Average	SD(b)	RSD, %(c)
3/09/84	10-100	5	0.97	0.18	18(d)
3/14/84	1-10	5	1.62	0.12	7.5
3/21/84	1-10	5	1.61	0.19	12
4/02/84	10-100	4	1.57	0.10	6.5
4/04/84	1-10	3	1.73	0.08	4.6

(a) Number of calibration standards analyzed on the given day.
(b) SD = Standard Deviation.
(c) RSD, % = Percent Relative Standard.
(d) Internal standard method provided less reliable results for this data set due to a procedural error. See discussion in Section 5, Reagent Water.

TABLE 20. INTERNAL STANDARD CALIBRATION RESPONSE FACTORS FOR ACRYLONITRILE

Date of Analysis	Calibration Range, µg/L	N(a)	Response Factor Parameter Average	SD(b)	RSD, %(c)
3/09/84	10-100	5	0.69	0.09	13(d)
3/14/84	1-10	5	0.88	0.06	6.4
3/21/84	1-10	5	0.93	0.02	1.7
4/02/94	10-100	4	0.92	0.06	6.5
4/04/84	1-10	3	0.96	0.09	9.9

(a) Number of calibration standards analyzed on the given day.
(b) SD = Standard Deviation.
(c) RSD, % = Percent Relative Standard Deviation.
(d) Internal standard method provided less reliable results for this data set due to a procedural error. See discussion in Section 5, Reagent Water.

REFERENCES

1. Manual of Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA-600/4-82-057, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 43268, July 1982.

2. Evaluation of Office of Solid Waste Methods 8030 and 8090. Report for U.S. Environmental Protection Agency Contract No. 68-03-1760, Work Assignment 3 (in preparation).

3. Glaser, J. A., Foerst, D. L., McKee, G. D., Quave, S. A., and Budde, W. L., "Trace Analyses for Wastewaters", Environmental Science and Technology, 15, 1426 (1981).

APPENDIX

U.S. EPA METHOD 603

(1982 Version)

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

Acrolein and Acrylonitrile—Method 603

1. Scope and Application

1.1 This method covers the determination of acrolein and acrylonitrile. The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
Acrolein	34210	107-02-8
Acrylonitrile	34215	107-13-1

1.2 This is a purge and trap gas chromatographic method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for either or both of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 624 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for the parameters listed above, if used with the purge and trap conditions described in this method.

1.3 The method detection limit (MDL, defined in Section 12.1)[1] for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5

1.5 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system and a gas chromatograph (GC) and in the interpretation of GC chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 An inert gas is bubbled through a 5-mL water sample contained in a heated purging chamber. Acrolein and acrylonitrile are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the analytes are trapped. After the purge is completed, the trap is heated and backflushed with the inert gas to desorb the compounds onto a gas chromatographic column. The gas chromatograph is temperature

programmed to separate the analytes which are then detected with a flame ionization detector [2,3].

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the compounds of interest from the interferences that may occur.

3. Interferences

3.1 Impurities in the purge gas and organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.5. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high analyte levels, it may be necessary to wash out the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105 °C oven between analyses. The trap and other parts of the system are also subject to contamination, therefore, frequent bakeout and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[4-6] for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial—25-mL capacity or larger, equipped with a screw cap with a hole in the center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water and dry at 105 °C before use.

5.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C for one hour before use.

5.2 Purge and trap device—The purge and trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are now commercially available.

5.2.1 The sample purger must be designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purge device must be capable of being heated to 85 °C within 3.0 minutes after transfer of the sample to the purge device and being held at 85 ± 2 °C during purge cycle. The entire water column in the purge device must be heated. Design of this modification to the standard purge device is optional, however, use of a water bath is suggested.

5.2.1.1 Heating mantle—To be used to heat water bath.

5.2.1.2 Temperature controller—equipped with thermocouple/sensor to accurately control water bath temperature to ± 2 °C. The sample purger illustrated in Figure 1 meets these design criteria.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. The trap must be packed to contain 1.0 cm of methyl silicone coated packing (Section 6.5.2) and 23 cm of 2,6-diphenylene oxide polymer (Section 6.5.1). The minimum specifications for the trap are illustrated in Figure 2.

5.2.3 The desorber must be capable of rapidly heating the trap to 100 °C. The polymer section of the trap should not be heated higher than 180 °C. The desorber, illustrated in Figure 2, meets these design criteria.

5.2.4 The purge and trap device may be assembled as a separate unit as illustrated in Figure 3 or be coupled to a gas chromatograph.

5.3 pH paper—Narrow pH range, about 3.5 to 5.5 (Fisher Scientific Short Range Alkacid No. 2, #14-837-2 or equivalent).

5.4 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.4.1 Column 1—6 ft long × 0.1 in ID stainless steel or glass, packed with Durapak-Carbowax 400/Porasil-C (100/120 mesh) or equivalent. This column was used to develop the method performance statements given in Section 12. Guidelines for the use of alternate column packings are provided in Section 10.1.

5.4.2 Column 2—6 ft long × 0.1 in ID stainless steel or glass, packed with Chromosorb 101 (60/80 mesh) or equivalent.

5.4.3 Detector—Flame ionization. This type of detector has proven effective in the analysis of wastewaters for the parameters listed in the scope, and was used to develop the method performance statements in Section 12. Guidelines for the use of alternate detectors are provided in Section 10.1.

5.5 Syringes—5-mL, glass hypodermic with Luerlok tip (two each).

5.6 Micro syringes—25 µL.

5.7 Syringe valve, 2-way with Luer ends (three each).

5.8 Bottle—15-mL screw-cap with Teflon cap liner.

5.9 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.1.1 Reagent water can be generated by passing tap water through a carbon filter bed containing about one pound of activated carbon (Filtrasorb-300 or equivalent, Calgon Corp).

6.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle and seal with a Teflon lined septum and cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Sodium hydroxide solution (10 N)—Dissolve 40 g NaOH in reagent water and dilute to 100 mL.

6.4 Hydrochloric acid solution (1 + 1)—Slowly add 50 mL concentrated HCl to 50 mL reagent water.

6.5 Trap Materials

6.5.1 2,6-Diphenylene oxide polymer, Tenax (60/80 mesh) chromatographic grade.

6.5.2 Methyl Silicone packing—3% OV-1 on Chromosorb-W (60/80 mesh) or equivalent.

6.6 Stock standard solutions—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in reagent water using assayed liquids. Since acrolein and acrylonitrile are lachrymators, primary dilutions of these compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

6.6.1 Place about 9.8 mL of reagent water into a 10-mL ground glass stoppered volumetric flask. For acrolein standards the reagent water must be adjusted to pH 4 to 5. Weigh the flask to the nearest 0.1 mg.

6.6.2 Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the water without contacting the neck of the flask.

6.6.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.6.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4 °C and protect from light.

6.6.5 Prepare fresh standards weekly.

6.7 Secondary dilution standards—Using stock standard solutions, prepare secondary dilution standards in reagent water that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sections 7.3.1 or 7.4.1 will bracket the working range of the analytical system. Secondary dilution standards should be prepared weekly and stored at 4 °C. They should be checked frequently for signs of degradation or evaporation. Quality control check standards that can be used to determine the accuracy of calibration standards will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, in Cincinnati, Ohio.

7. Calibration

7.1 Assemble a purge and trap device that meets the specifications in Section 5.2. Condition the trap overnight at 180 °C by backflushing with an inert gas flow of at least 20 mL/min. Prior to use, daily condition traps 10 minutes while backflushing at 180 °C.

7.2 Connect the purge and trap device to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate parameters equivalent to those in Table 1. Calibrate the purge and trap-gas chromatographic system using either the external standard technique (Section 7.3) or the internal standard technique (Section 7.4).

7.3 External standard calibration procedure:

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 µL of one or more secondary dilution standards to 100, 500, or 1000 mL of reagent water. A 25-µL syringe should be used for this operation. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These standards must be prepared fresh daily.

7.3.2 Analyze each calibration standard according to Section 10, and tabulate peak height or area responses versus the concentration of the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (≤10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.4 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.4.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.3.1.

7.4.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 6.6 and 6.7. It is recommended that the secondary

dilution standard be prepared at a concentration of 15 µg/mL of each internal standard compound. The addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 µg/L.

7.4.3 Analyze each calibration standard according to Section 10 adding 10 L of internal standard spiking solution directly to the syringe (Section 10.4). Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using equation 1.

$$\text{Eq. 1 } RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard.
C_s = Concentration of the parameter to be measured.

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF.

7.4.4 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a representative spike concentration for each compound to be measured. Using stock standards, prepare a quality control check sample concentrate in reagent water 500 times more concentrated than the selected concentrations. Quality control check sample concentrates, appropriate for use with this method, will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

8.2.2 Using a syringe, add 10 µL of the check sample concentrate to each of a minimum of four 5-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using Table 2, note the average recovery (X) and standard deviation (p) expected for each method parameter. Compare these to the calculated values for R and s. If $s > 2p$ or $|X - R| > 2p$, review potential problem areas and repeat the test.

8.2.5 The U.S. Environmental Protection Agency plans to establish performance criteria for R and s based upon the results of interlaboratory testing. When they become available, these criteria must be met before any samples may be analyzed.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R − 3s

where R and s are calculated as in Sections 8.2.3.

The UCL and LCL can be used to construct control charts[7] that are useful in observing trends in performance. The control limits above must be replaced by method performance criteria as they become available from the U.S. Environmental Protection Agency.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly[7].

8.4 The laboratory is required to collect a portion of their samples in duplicate to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 11.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Each day, the analyst must demonstrate through the analysis of reagent water, that interferences from the analytical system are under control.

8.6 It is recommended that the laboratory adopt additional quality

assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 The samples must be iced or refrigerated from the time of collection until extraction. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site. EPA methods 330.4 and 330.5 may be used for measurement of chlorine residual[8]. Field test kits are available for this purpose.

9.2 If acrolein is to be analyzed, collect about 500 mL sample in a clean glass container. Adjust the pH of the sample to 4 to 5 using acid or base, measuring with narrow range pH paper. Samples for acrolein analysis receiving no pH adjustment must be analyze within three days of sampling.

9.3. Fill a sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If preservative has been added, shake vigorously for one minute. Maintain the hermetic seal on the sample bottle until time of analysis.

9.4 All samples must be analyzed within 14 days of collection[3].

10. Sample Extraction and Gas Chromatography

10.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this Table are estimated retention times and MDL that can be achieved by this method. An example of the separations achieved by Column 1 is shown in Figure 4. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

10.2 Calibrate the system daily as described in Section 7.

10.3 Adjust the purge gas (nitrogen or helium) flow rate to 20 mL/min. Attach the trap inlet to the purging device, and set the device to purge. Open the syringe valve located on the purging device sample introduction needle.

10.4 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 10.0 µL of the internal standard spiking solution (Section 7.4.2), if applicable, through the valve bore then close the valve.

10.5 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

10.6 Close both valves and purge the sample for 15.0 ± 0.1 minutes while heating at 85 ± 2 °C.

10.7 After the 15-minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Begin the temperature program for the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 100 ± 10 °C while backflushing the trap with an inert gas between 20 and 60 mL/min for two minutes.

10.8 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-mL flushes of reagent water.

10.9 After desorbing the sample for 2.0 minutes recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 100 °C. After approximately seven minutes turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool the trap is ready for the next sample.

10.10 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11. Calculations

11.1 Determine the concentration of individual compounds in the sample.

11.1.1 If the external sample calibration procedure is used, calculate the concentration of material from the peak response using the calibration curve or calibration factor determined in Section 7.3.2.

11.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.4.2 and the equation 2:

Eq. 2

Concentration $\mu g/L = (A_s C_{is})/(A_{is})(RF)$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard.

11.2 Report results in micrograms per liter. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

11.3 For samples processed as part of a set where the spiked sample recovery falls outside of the control limits in 8.3, data for the affected parameters must be labeled as suspect.

12. Method Performance

12.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero[1]. The MDL concentrations listed in Table 1 were obtained using reagent water[9]. Similar results were achieved using representative wastewaters.

12.2 This method is recommended for the concentration range from the MDL up to 1000 × MDL. Direct aqueous injection techniques should be used to measure concentration levels above 1000 × MDL.

12.3 In a single laboratory (EMSL-CI), using spiked wastewater, the average recoveries presented in Table 2 were obtained[3]. Seven replicate spiked samples were analyzed for each parameter. The relative standard deviation of the measurement is also included in Table 2.

12.4 The U.S. Environmental Protection Agency is in the process of conducting an interlaboratory method study to fully define the performance of this method.

References

1. See Appendix A.
2. Bellar, T.A., and Lichtenberg, J.J. *Journal American Water Works Association, 66,* 739, (1974).
3. Kerns, E.H., et al, "Determination of Acrolein and Acrylonitrile in Water by Heated Purge and Trap Technique," 1980, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.
4. "Carcinogens—Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health. Publication No. 77-206, Aug. 1977.
5. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).
6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
7. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory—Cincinnati, Ohio 45268, March 1979.
8. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory—Cincinnati, Ohio 45268. March 1979.
9. "EPA Method Validation Study 25, Method 603 (Acrolein and Acrylonitrile)," Report for EPA Contract 68-03-2856 (In preparation).

Table 1. *Chromatographic Conditions and Method Detection Limits*

Parameter	Retention Time (min.) Column 1	Retention Time (min.) Column 2	Method Detection Limit µg/L
Acrolein	*9.2*	*8.2*	*0.6*
Acrylonitrile	*13.5*	*9.8*	*0.5*

Method detection limit based upon recovery of 5.0 µg/L dose into tap water.

Column 1 conditions: Durapak Carbowax 400/Porasil C, (100/120 mesh) packed in a 6 ft × 0.1 in. ID stainless steel or glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held at 45 °C for 2 min, then programmed at 8 °C/min to 85 °C and held for 12 min. The column temperature should then be raised to 120 °C for 7 minutes to bake out water. Failure to dry the column may lead to irreproducable retention times[9].

Column 2 conditions: Chromosorb 101, (60/80 mesh) packed in a 6 ft x 0.1 in ID stainless steel, glass column with helium carrier gas at 40 mL/min flow rate. Column temperature held at 80°C for 4 min. then programmed at 15°C/min to 120°C and held 12 min.

Table 2. *Single Operator Accuracy and Precision*

Parameter	Average Percent Recovery	Standard Deviation %	Spike Range (µg/L)	Number of Analyses	Matrix Types
Acrolein	*96*	*11.6*	*20*	*7*	*1*
Acrylonitrile	*107*	*5.6*	*20*	*7*	*1*

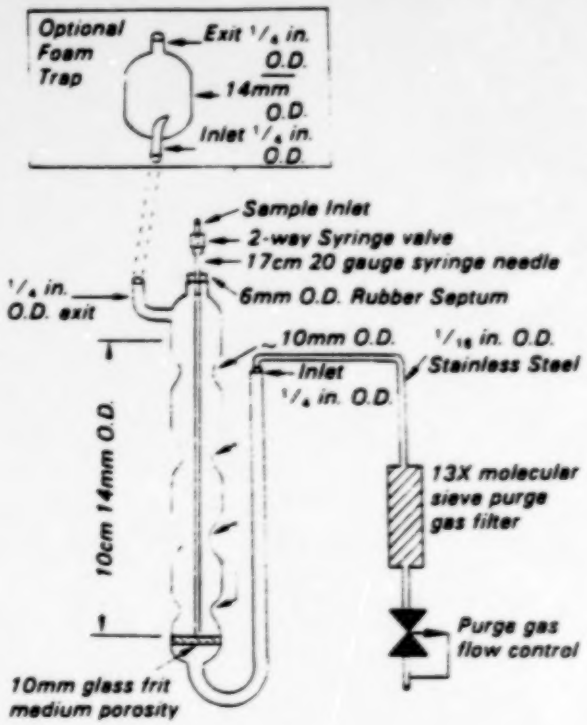

Figure 1. *Purging device*

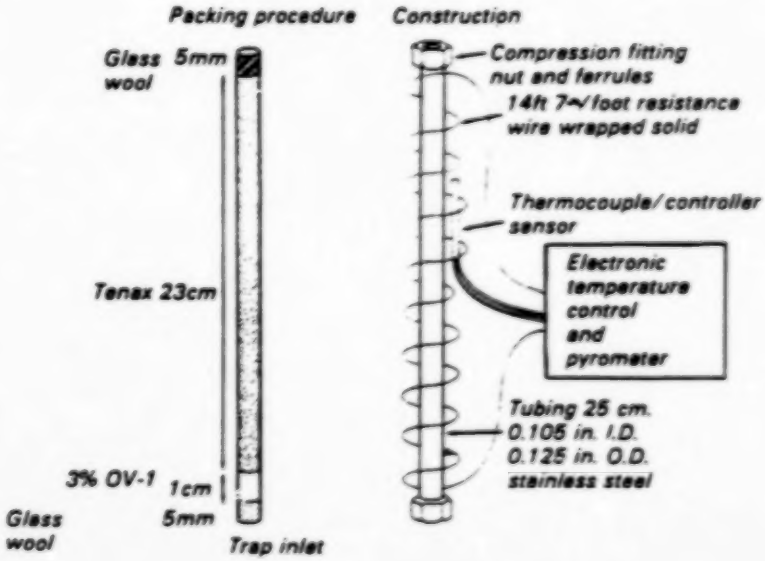

Figure 2. *Trap packings and construction to include desorb capability*

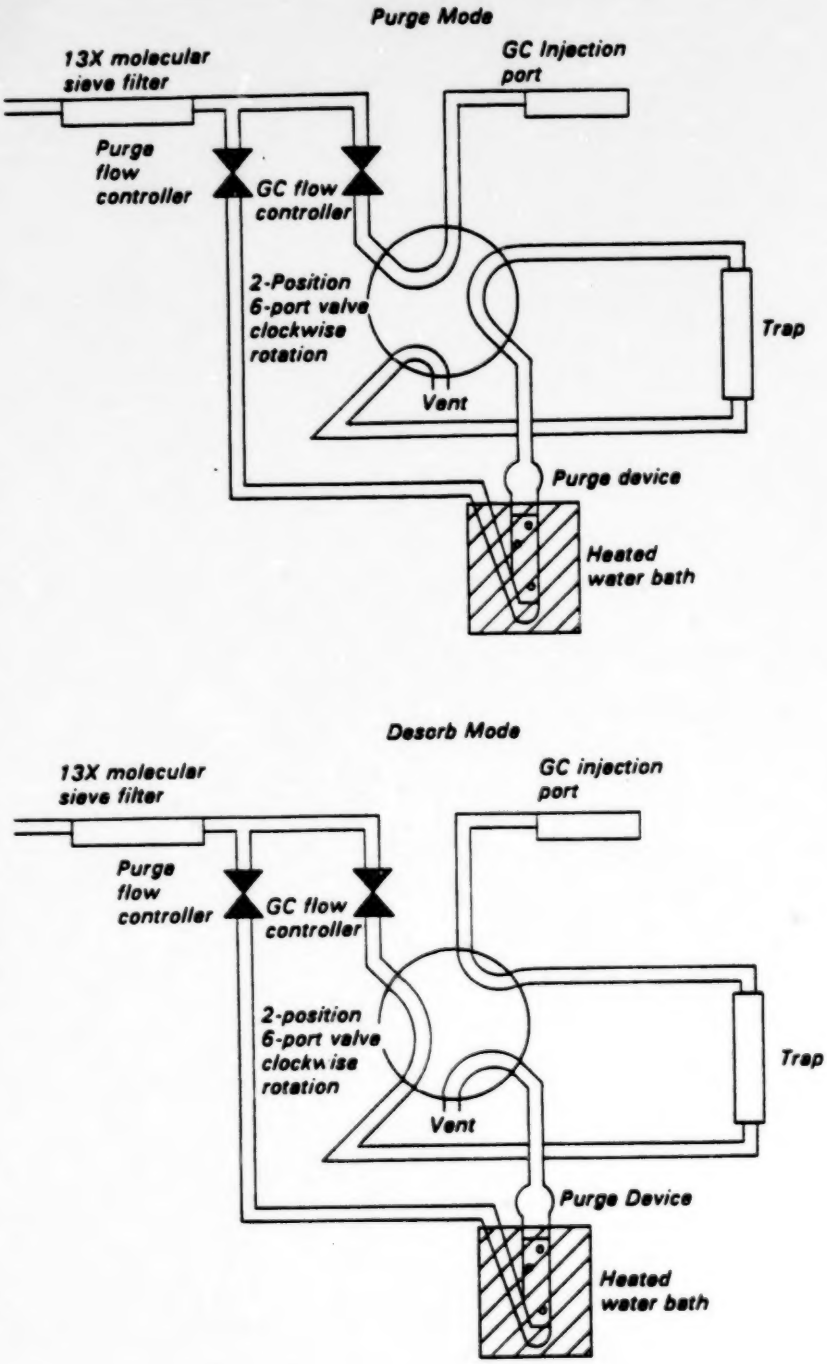

Figure 3. *Schematic of heated purge and trap device*

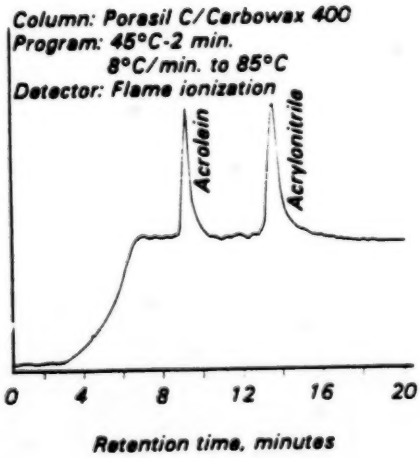

Figure 4. *Gas chromatogram of acrolein and acrylonitrile*